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MECHANISMS FOR ENERGY SHIFTS OF ATOMIC K x RAYS

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1. INTRODUCTION

The energies of the K-series x rays (Fig. 1) are for a given element almost independent of the source and the mode of excitation. Nevertheless, by means of suitably designed spectrometers, to be discussed in Section 2, it is possible to observe minute energy shifts. The main part of the present paper is devoted to experiments in which such shifts are observed, and to their interpretation.

There is a double aim behind the study of x-ray energy shifts. First of all, the experiments can be designed to exclude certain mechanisms and to be sensitive to others. In this way it is possible to test our understanding of the processes involved; several contributions that had not been considered in earlier work have in the last few years been recognized. A second reason for investigating shifts is that they provide new probes for studying nuclei, atoms, and solids.

We give a short account of the mechanisms to be discussed. The first two have been known for a long time and have been reviewed in detail elsewhere; we nevertheless mention them briefly, both for the sake of completeness and because they give additional contributions when some of the other mechanisms are studied.

Fig. 1 Origin and nomenclature for the K-series x rays. The energy scale is for the case of holmium ($Z = 67$).

- i) Isotope shifts. They originate from the effect of finite nuclear size on the $1s$ binding energy (Section 3).
- ii) Chemical shifts. They originate from changes in the atomic screening. These changes are caused by outer electrons participating in the formation of chemical bonds (Section 4).
- iii) Hyperfine shifts. For $1s^{-1}$ excitations caused by radioactive decays, intensity rules related to the total atomic angular momentum F lead to shifts that may reach several eV. These shifts furnish a method for measuring nuclear magnetic moments (Section 5) and maybe also for determining multipole mixing of beta transitions.
- iv) Dynamic shifts. Outer-shell excitations associated with the excitation mechanism modify temporarily the atomic screening and give rise to small shifts (Section 6).
- v) Atomic-structure shifts. Nuclear beta-decay transforms an element into a neighbouring one but preserves temporarily the electronic structure of the mother atom. Structural differences influence (via the screening) the x-ray energies in a characteristic way that is not yet fully understood (Section 7).
- vi) Other contributions (Section 8).

Finally, we remind the reader that there has been remarkable progress in the understanding of absolute x-ray energies, and that contributions at the eV level can no longer be disregarded entirely. Improved experimental methods (Borchert, 1976; Borchert *et al.*, 1980c; Deslattes and Kessler, 1982) and more refined theoretical calculations (Chen *et al.*, 1981) now give agreement to within 1–2 eV for the K x-ray energies of heavier elements corresponding to a precision of $1-2 \times 10^{-5}$.

2. THE EXPERIMENTAL METHOD

The energy shifts of K x-ray lines dealt with here are very small in comparison with their natural widths Γ_{nat} (Nelson *et al.*, 1969, 1970, Krause and Oliver, 1979). Diffraction spectrometers which have the highest resolving power are therefore used for x-ray shift measurements. Improvements in crystal diffraction spectroscopy during the last two

decades have been described by Knowles (1979). Since then, progress has continued, and very high resolving powers have been obtained not only with a double-flat crystal spectrometer (Deslattes and Kessler, 1979) but also with curved crystal diffractometers where either a favourable lattice plane has been chosen (Koch *et al.*, 1980) or where the crystal lamina was cut out of the crystal block in the optimum way so that bending of the lamina did not distort the lattice planes (Sumbaev, 1957, 1959; Sumbaev and Lapin, 1980).

The use of curved crystals in focusing diffraction spectrometers (Cauchois, 1932a) results in an increase of the counting rate by about three orders of magnitude. For the spectroscopy of radiation from very small sources it is advisable to employ the DuMond geometry (DuMond, 1947), which has been successfully utilized by various groups (Boehm, 1975; Brockmeier *et al.*, 1965; Van Eijk and Schutte, 1970; Van Eijk and Vissher, 1970; Borchert *et al.*, 1981b) for isotope shift measurements and for studies of other mechanisms for energy shifts in atomic K x-ray spectra (Boehm, 1975; Borchert *et al.*, 1977, 1978a, 1978b; Hansen *et al.*, 1981; Borchert *et al.*, 1980b). Figure 2 shows the x-ray beam geometry of the DuMond type spectrometer (Borchert *et al.*, 1980a) installed for x-ray energy shift studies at CERN. In cases where larger sources are available, the Cauchois geometry (Cauchois, 1932a, 1932b) can be used as well. In fact, the x-ray energy shift measurements by the groups of Boehm (Chesler and Boehm, 1968; Boehm, 1975; Bhattacharjee *et al.*, 1969; Lee and Boehm, 1973; Boehm and Lee, 1974) and Sumbaev (Sumbaev and Mezentssev, 1965a, 1965b; Sumbaev *et al.*, 1969; Smirnov *et al.*, 1969; Ryl'nikov *et al.*, 1972; Sumbaev, 1976; Molkanov *et al.*, 1976; Egorov *et al.*, 1978; Sumbaev, 1978) have been carried out with Cauchois spectrometers, where the x-ray beam direction is reversed with respect to the one depicted in Fig. 2. Descriptions of such spectrometers can

Fig. 2 Measurements of very small x-ray energy shifts are carried out with high-resolution curved-crystal spectrometers. The upper part of the figure shows the principle of the DuMond geometry (DuMond, 1947) with a narrow source (S) and an extended detector (NaI). Reversed beam direction is characteristic of the Cauchois geometry (Cauchois, 1932a) with an extended source at the NaI position and a narrow detector at S. The lower part of the figure shows more details of the sources used with the DuMond-type spectrometer at CERN. At the left, the photoionization source (¹⁶⁹Yb) arrangement is shown as it was employed during isotope shift measurements (Borchert *et al.*, 1981b). At the right side is the set-up as used during the measurements of hyperfine shifts (Borchert *et al.*, 1977). For measurements of other shifts, only one x-ray source was photoionized by a smaller Yb source, the other source emitting x rays excited through its own decay.

Fig. 3 Typical K x-ray spectrum as emitted during the electron capture beta decay of ^{189}Ir . The measured width of the $K\alpha_1$ line is only 18% larger than the natural line width (Nelson *et al.*, 1969, 1970). This increase is due to the geometrical width of the source and the defocusing width of the curved crystal. These contributions alone yield the line width of the 69.5 keV γ transition. Recent measurements also include the determination of the shift of the K0 "line" which constitutes electron transitions from shells with main quantum number $n \geq 5$ to the K shell ($n = 1$).

be found in various publications (Seppi *et al.*, 1962; Boehm, 1975; Chesler and Boehm, 1968; Henrikson and Boehm, 1974; Sumbaev, 1978). For a given curved crystal and optimized geometries, the counting rate in the DuMond-type set-up equals that of the Cauchois geometry. The latter even permits a spectrograph mode of operation if a suitable position-sensitive detector is available, so that a segment of the spectrum can be recorded simultaneously. The Cauchois spectrometer allows the use of a very narrow detector which minimizes background, but it needs larger sources which must be prepared so that the required homogeneity is obtained. These sources are 2–3 orders of magnitude more active than the very narrow sources of a DuMond spectrometer. The DuMond geometry is preferable for measurements with rare isotopes which are available only in small quantities, and in cases where very small sources are produced, e.g. through the collection of radionuclides (Borchert *et al.*, 1977) obtained at isotope separators (Ravn, 1979). The larger detector in a DuMond spectrometer gives a higher background and requires better shielding.

In order to obtain data with the highest statistical quality for a given measuring time, the experiment should be carried out under optimized conditions (Schult, 1965). This implies that the source width in a DuMond spectrometer or the detector-slit width in a Cauchois spectrograph are in proper relation to the geometrical width of the x-ray line at the position S of Fig. 2. The reflection power of the crystal can be maximized if the crystal plate is cut out of the block in the right way so that the lattice planes are curved when the crystal is bent (Sumbaev and Smirnov, 1963). Alternatively, the reflectivity can be increased by application of electric fields (Dousse and Kern, 1976). Under optimum conditions the combination of the width of the source (slit) at S of Fig. 2 and of the defocusing width of the curved crystal, together with the width of the crystal diffraction pattern for the x-ray energy, yields a total width for a γ -ray reflection smaller than that for the x-ray line reflection, because of the natural line width Γ_{nat} of the x ray (Fig. 3).

The x-ray shifts can be as small as 10^{-3} of the natural line width, and their measurement requires great care. Instead of measuring absolute x-ray energies E_x with an accuracy of $10^{-7} \times E_x$, the x-ray energy shift can be obtained much more easily through a relative measurement, namely of the difference between the energies of one x-ray line emitted from two or more samples (Lee and Boehm, 1973; Sumbaev, 1978; Borchert *et al.*, 1980a).

For this purpose a measurement strategy is adopted by which systematic errors are efficiently eliminated so that the uncertainty in the shift measurement is essentially due to the statistical error. For shift measurements with Cauchois spectrometers, samples containing 0.1–2 g of material were pressed into pills and fluorescence-excited by means of an x-ray tube or a ^{169}Yb source of 200 Ci (Chesler and Boehm, 1968; Boehm, 1975; Sumbaev, 1978). The samples were carefully controlled for homogeneity and chemical purity (Boehm, 1975), and part of the aberrational shift from the remaining inhomogeneous source distribution was compensated (Sumbaev and Mezentsev, 1965b; Boehm, 1975) by spinning the sample about an axis through its center. The samples were brought into the source position alternatively with a suitable source-changing device (Boehm, 1968; Sumbaev, 1978). Many source changes were carried out with the detector slit fixed at the measuring angle θ , and θ was subsequently changed to the next measuring position. The DuMond geometry also permits the exchange of small sources (Brockmeier *et al.*, 1965) or

the installation of a defining slit (Van Eijk and Schutte, 1970) very close to a slightly larger source. The geometrical reproducibility in this case has to be $\sim 10 \mu\text{m}$, which is not easily assured by a mechanical source-changing mechanism.

Another solution, suggested by the smallness of the sources, is to mount the two samples slightly above and below the ideal source point S in the symmetry plane of the spectrometer, as shown in Fig. 2. Aberrations increase quadratically with the distance from S , hence they vanish for geometrically identical sources at equal distances above and below the symmetry plane. Small inhomogeneities lead to aberrations which are negligible in comparison with statistical errors for sources at close distance and, in addition, they can be essentially eliminated by an additional measurement with the sources interchanged (Fig. 2). The symmetry plane is determined experimentally by verifying that identical sources give a null result. Typical sources at the CERN-DuMond spectrometer (Borchert *et al.*, 1980a) were $\lesssim 5 \text{ mm}$ high, $\lesssim 2 \text{ mm}$ in the direction of the x-ray beam, and $\lesssim 0.15 \text{ mm}$ in the direction of the dispersion of the spectrometer. Photoionization (PI) was induced with a ^{169}Yb source of up to 50 Ci. For each measuring point a shutter is moved back and forth many times in the direction of the dispersion; this transmits the beam from only one source at a time to the spectrometer for periods which can be chosen so that the statistical accuracy in the shift measurement is maximal. The rapid cycling at the same time eliminates the effects of drift of the apparatus. The two sources were adjusted to yield well-overlapping x-ray reflections, as shown in Fig. 4. The shift arising from the (inevitable) residual displacement is corrected through the measurement of the reflections at positive (+) and negative (−) Bragg angles, θ . The point is that a mechanical displacement shifts both Bragg reflections by $\delta\theta_{\text{displ}}$ in the same direction so that their distance remains constant,

$$(\theta^+ + \delta\theta_{\text{displ}}) - (\theta^- + \delta\theta_{\text{displ}}) = \theta^+ - \theta^- ,$$

while their center of gravity is shifted by $\delta\theta_{\text{displ}}$. On the other hand, an energy change shifts the Bragg reflections by $\delta\theta_{\text{energy}}$ in opposite directions so that their center of gravity remains fixed while their distance changes from

$$\theta^+ - \theta^-$$

to

$$(\theta^+ + \delta\theta_{\text{energy}}) - (\theta^- - \delta\theta_{\text{energy}}) = \theta^+ - \theta^- + 2\delta\theta_{\text{energy}} .$$

The measurement of the x-ray energy shift then consists of a series of scans (each containing ~ 20 measuring points) across the pair of x-ray reflections at θ^+ , θ^- , θ^+ , θ^- , ... until the desired statistical accuracy is obtained. In a similar way, shift measurements are performed with a Cauchois spectrometer, where many source changes are carried out at each measuring point.

Because of the smallness of the shifts compared with the experimental line widths, the method of data reduction must be such that it does not introduce artificial shifts. Various methods have been applied (Boehm, 1975; Sumbaev, 1976, 1978; Hansen, 1978; Borchert *et al.*, 1980a). The best way to be sure of avoiding artificial shifts is to check that different approaches give consistent results (Borchert *et al.*, 1982).

Fig. 4 Reflections of the $K\alpha_1$ lines of ^{204}Pb and ^{208}Pb recorded at positive and negative Bragg angles with the DuMond-type diffraction spectrometer at CERN. The measuring time per point was 4 minutes.

3. THE ISOTOPE SHIFT

The shift in the x-ray energy when δA neutrons are added to an isotope with mass number A is referred to as the isotope shift. For heavier nuclei the energy change is approximately proportional to the variation in the mean square charge radius $\delta\langle r^2 \rangle_{A, A+\delta A}$. The largest shifts are observed for the K x rays, and arise in the $1s_{1/2}$ level while the contributions from the p levels are negligible (Boehm, 1975; Lee and Boehm, 1973). For this reason measurements of isotope shifts concentrate on $K\alpha_1$, the most intense of the K x rays.

K x-ray isotope shift measurements (Boehm, 1975) can be carried out in the absence of other shifts. Chemical shifts (Sumbaev, 1976) are avoided if the isotopically enriched samples exist in identical and stable forms with the same structure (Chesler and Boehm, 1968). Shake-off (Borchert *et al.*, 1978a) and other mechanisms (Borchert *et al.*, 1978b) can be eliminated if all samples are excited through photoionization. The full shift is the sum of the Coulomb shift, the mass shift, and the nuclear polarization shift,

$$\delta E(1s_{1/2}) = \delta E(K\alpha_1) = \delta E_{\text{Coul}} + \delta E_{\text{mass}} + \delta E_{\text{polar}}.$$

The total mass shift [the sum of the normal and specific mass shifts (Boehm, 1975; Boehm, 1968)] can be approximated (Chesler and Boehm, 1968; Sumbaev *et al.*, 1969; Boehm and Lee, 1974) by

$$\delta E_{\text{mass}, A \rightarrow A+\delta A} \approx -2/3(\delta A/1836 A^2) E(K\alpha_1).$$

The mass shift for heavy elements is very small in comparison with the measurement errors: for Pb, $\delta E_{\text{mass}, A \rightarrow A+1} \approx -0.7$ meV.

The influence of nuclear polarization (Breit, 1957) by the electron is also small (Reiner and Wilets, 1962), and according to recent calculations (Hoffmann *et al.*, 1982) it is completely negligible.

As discussed in greater detail by Seltzer (1969), it is useful to introduce the rapidly converging series

$$\delta E_{\text{Coul}} = \sum C_n \delta\langle r^{2n} \rangle = C_1 \lambda,$$

where the parameter λ thus defined usually deviates by less than 10% from $\delta\langle r^2 \rangle$.

The advantage of the electronic x-ray isotope shift measurement is its insensitivity to nuclear polarization, in contrast to muonic x-ray isotope shift measurements in which the nuclear polarization shift (Rinker and Speth, 1978) is not only a large fraction of the measured shift (Kessler *et al.*, 1975) but also is difficult to explain (Yamazaki *et al.*, 1979). Furthermore, the total mass shift is very small and the electronic part of the calculation (Seltzer, 1969) can be carried out with good accuracy. Optical isotope shift measurements (Manning *et al.*, 1950; Brix *et al.*, 1952; Steudel, 1952; Blaise, 1958; Heilig and Steudel, 1974; Moscatelli *et al.*, 1982) suffer from our insufficient knowledge of the specific mass shift, which is essential here. Furthermore, the electronic calculations of the initial and final states are, in general, not precise enough to give an accurate value for the λ parameter. For these reasons, the K x-ray isotope shifts serve for the normalization of optical data (Van Eijk and Vissher, 1970; Van Eijk and Schutte, 1970; Merton, 1919; Korostyleva, 1957; Brix and Kopfermann, 1958; Stacey, 1966; Golovin and Striganov, 1967; Boehm, 1975; Lee and Boehm, 1971; Heilig and Steudel, 1974; Lee *et al.*, 1978; Borchert *et al.*, 1982). A plot of the shifts of the $K\alpha_1$ line versus the shifts of an optical line (e.g. Fig. 5), yields for negligible mass shift (Stacey, 1966) the electronic factor C_1 for

Fig. 5 Comparison of the Coulomb energy shifts of the $K\alpha_1$ x-ray line with the optical isotope shifts of the 283.3-nm line (Thompson *et al.*, 1982) measured for ^{207}Pb , ^{206}Pb , and ^{204}Pb , each with respect to ^{208}Pb . The Coulomb energy shift allows for the small mass shift of the $K\alpha_1$ line. The mass shift of the optical transition is unknown but is assumed to be small in heavy elements (Stacey, 1966). The figure serves to test this aspect: for a negligible mass shift of the 283-nm line the optical isotope shifts should be proportional to the $K\alpha_1$ Coulomb shifts. Whilst the uncertainties of the optical data correspond to the widths of the data bars, their lengths equal twice the errors of the x-ray energy shifts. Unfortunately, the x-ray energy shifts cannot be measured much more accurately. Therefore, the data are only consistent with negligible mass shift in the optical data.

Fig. 6 The measurements of x-ray isotope shifts or optical isotope shifts yield the nuclear parameter λ (Seltzer, 1969) which is related to the shift δ of the mean square charge radius $\langle r^2 \rangle$. The figure shows these quantities for a few lead isotopes relative to ^{208}Pb . The data for ^{204}Pb , ^{206}Pb , and ^{207}Pb are from the $K\alpha_1$ x-ray shifts (Lee and Boehm, 1973; Borchert *et al.*, 1982) and those for ^{205}Pb and ^{210}Pb are from optical isotope shift measurements of the 283-nm line (Thompson *et al.*, 1982) and the 405-nm line (Brix *et al.*, 1952), respectively. Because of the large uncertainties in the calculation of the electron wave functions at the nuclear site, the optical shifts were normalized with the use of the x-ray shift data. This normalization was accomplished once with the assumption of zero optical mass shift (left data bar for ^{205}Pb and ^{210}Pb) and once for a mass shift as obtained from the fit to the x-ray data (right data bars).

the optical transition. Combining this parameter with optical-shift data for unstable isotopes (Brix *et al.*, 1952; Thompson *et al.*, 1982; Moscatelli *et al.*, 1982), it is possible to determine the nuclear radius also for unstable isotopes, as shown in the example in Fig. 6. Isotope shifts of x rays have been measured in many cases (Brockmeier *et al.*, 1965; Boehm, 1975; Bhattacharjee *et al.*, 1968; Boehm, 1968; Chesler and Boehm, 1968; Bhattacharjee *et al.*, 1969; Lee and Boehm, 1971, 1973; Lee *et al.*, 1978; Boehm and Lee, 1974; Sumbaev and Mezentssev, 1965a; Sumbaev *et al.*, 1969; Ryl'nikov *et al.*, 1972). The K x-ray data have contributed in an important way to the understanding of nuclear radii (Boehm, 1975, 1968; Lee and Boehm, 1971; Bhattacharjee *et al.*, 1968; Uher and Sorensen, 1966). Space does not permit a detailed discussion of this subject here; we shall simply give some recent references and point to the important interplay of the x-ray data with those from optical spectra, electron scattering, and muonic x rays. Recently, x-ray shift data (Borchert *et al.*, 1981a) of the stable lead isotopes have been compared with the droplet model (Myers, 1969; Myers and Swiatecki, 1974; Myers, 1977) and with $\delta\langle r^2 \rangle$ values calculated in the framework of the shell model (Speth *et al.*, 1974; Borchert *et al.*, 1982). Although the general agreement is rather good, the odd-even staggering is not explained. McGrory and Brown (1982) have discussed in detail the shell-model calculations of nuclear charge radii. Nuclear charge distributions have been dealt with elsewhere (Malaguti *et al.*, 1982).

The x-ray shift data have also been compared with the results from muonic isotope shift measurements (Boehm, 1975; Lee and Boehm, 1973; Lee *et al.*, 1978; Borchert *et al.*, 1982). For samarium isotopes, the comparison of muonic, optical, and electronic x-ray shifts shows good agreement (Powers *et al.*, 1979). For the mercury isotopes the optical data (Bonn *et al.*, 1976) indicate larger shifts than those given by the x-ray data (Lee *et al.*, 1978). This could be due to insufficient accuracy of the optical screening calculation. The muonic data (Hahn *et al.*, 1979) are consistent with the x-ray shifts except for ^{201}Hg , where the nuclear polarization correction of the muonic data seems to be the major source of error.

For the stable isotopes of lead, the shift between ^{208}Pb and ^{204}Pb , obtained from the muonic data alone, clearly disagrees with the shift derived from combining muonic data (Kessler *et al.*, 1975) with electron scattering data (Emrich *et al.*, 1981; Rychel, 1980; Fricke, private communication, 1981; Borchert *et al.*, 1982) when the nuclear polarization correction was applied as calculated by Skardhamar (1970). The combined ($\mu + e$) data are consistent with but systematically smaller than the electronic x-ray shift data.

Although most of the isotope shifts can be measured with an accuracy which is sufficient for the comparison with theory, at present all methods suffer from different limitations. The electronic K x-ray shifts, being very small compared with the line widths, cannot be measured with the desired accuracy. The muonic x-ray shifts are large and can be measured accurately, but the nuclear polarization adds a shift which cannot be calculated reliably. Optical isotope

shift measurements (Heilig and Steudel, 1974), which have been leading in the field for many decades (Brix, 1977, 1981, 1982) and which have opened up the possibility of measuring nuclear charge radii even of radioisotopes (Brix *et al.*, 1952), have benefited enormously from the introduction of laser techniques (Otten, 1981; Rebel, 1980; Rebel and Schatz, 1982; Timmermann, 1980; Lindgren *et al.*, 1981). Thanks to the combination of muonic, electronic x-ray, and optical data it is today possible to obtain a global picture of nuclear charge radii, including even isotopes far from stability (Otten, 1981; Thibault, 1981).

4. THE CHEMICAL SHIFT

Chemical shifts are observed as the differences in energies between x rays from a given element incorporated in different chemical compounds. For the lighter elements, in particular, the bonding effects may change the x-ray spectra in a major way as discussed by Nagel and Baun (1974). For the inner shells of the heavier elements, chemical shifts were believed to be negligible (Sandström, 1957), until Sumbaev and Mezentsev (1965a) reported shifts for the $K\alpha_1$ lines of molybdenum and tin. A large body of data has since accumulated and has been reviewed on several occasions by Sumbaev (1969, 1976, 1978) and by Boehm (1975). As the chemical shift is closely related to several phenomena to be discussed in the following, we give here a brief summary of its origin, key data, and applications.

4.1 Origin of the Chemical Shift

The discussion of chemical shifts (see, for example, Sumbaev, 1976) starts from the notion that a valence electron participating in the formation of a chemical bond is removed or "pulled away" from the atom. A decrease in the electronic screening ensues and leads to an increase in inner-shell binding energies; the *differences* in the binding energies are, however, much smaller, but the naïvely expected trend still is an increase in the x-ray energies. The real situation is more complicated as it is not sufficient to consider the direct interaction between the valence electron and the 1s and np states responsible for the K x-ray emission. Just to take an example, the direct effect would be close to zero for the case of a 4f electron (illustrated in Fig. 7); the fact that very large negative shifts are seen there arises from a readjustment ("compression") of the electron density distribution in the atom.

The chemical shifts can be treated in a somewhat more quantitative fashion by performing self-consistent-field calculations of the energy changes associated with the removal of an electron in a given atomic state (Sumbaev, 1969; Lee *et al.*, 1971, 1973; Petrovich *et al.*, 1971). These free-atom-ion calculations are still very far from representing a chemical bond, but may be expected to represent an extreme value, which is approached for strongly ionic bonds. It is possible to obtain a convincing semi-empirical presentation of the chemical shifts in metal/metal-oxide systems by introducing the concept of bond ionicities related to the difference in electronegativities of the partners in the compound (Sumbaev, 1969, 1976).

The 2p, 3p, 4p and 5p electrons are situated in different parts of the atom and undergo different chemical shifts. For this reason, the energy shifts of the $K\alpha_{1,2}$, $K\beta_{1,3}$, $K\beta_{2,4}$, and K0 lines characterize a valence electron by a "fingerprint" pattern.

4.2 Examples of Data and Applications

Examples of measured chemical shifts are shown in Fig. 7. The "fingerprints" are very clear for 4f electrons but relatively uncharacteristic for s, p, d electrons. For this reason, much work has centered on the rare-earth elements (see Sumbaev, 1978), and additional pertinence is lent to this research by the current interest in valence fluctuations.

Fig. 7 Examples of chemical shifts (from Sumbaev, 1976, 1978). The shift due to the removal of a 5s electron (the pair RbCl-Rb) is small and positive, whilst the shifts involving the removal of a 4f electron (rare-earth elements) are large and negative indicating the compression effect as the main source of the shift. The calculation of the 4f shift shown is based on a self-consistent free-atom-ion calculation.

The theoretical picture (Johansson and Rosengren, 1975) of valence change in the rare earths involves the transition of a localized (non-bonding) 4f electron into a delocalized (bonding) 5d6s state, i.e. one electron is promoted from the 4f state into the 5d6s conduction band. However, for the case of cerium, which under pressure undergoes a phase transition from the normal trivalent γ -phase to the more dense α -phase, this explanation seems to be ruled out by thermochemical data (Johansson, 1978). Instead it has been suggested (Johansson, 1974) that the γ - α transformation is due to a fundamental change of the f-state itself, a transition sometimes looked upon as a Mott transition. Such itinerant f-states are found among the earlier actinide metals (Johansson, 1975). It is therefore interesting that for the Ce α - γ phase transition the experiment of Shaburov *et al.* (1973) shows a "fingerprint" (Fig. 7) that would agree with a decrease in the 4f occupancy by 0.5 electron. However, it is not yet clear whether the experiment is at variance with the Mott transition picture. Further experimental data would be welcome.

The problem, however, is of interest not only to solid-state physicists. Inasmuch as the standard state for experimental x-ray energies is the metallic state (see the article by Deslattes and Kessler, this volume) while theoretical calculations are carried out for free atoms (see, for example, Chen *et al.*, 1981), the possible existence of shifts related to the electronic structure of metals could eventually become important for the understanding of absolute x-ray energies. In Section 7.4 we mention data for the 5d elements that may point in this direction. The subject of shifts in binding energies of core electrons between free atoms and the atoms in the metallic state is one that has been widely studied, theoretically and also experimentally, especially in photoionization experiments. The shifts dealt with in the present paper correspond to *differences* in core level shifts for very deep-lying states. Being small, their existence would not necessarily be negated by the success of a semi-empirical theory of core-level shifts, which does not invoke any details of the internal electronic structure (Johansson and Mårtensson, 1980).

5. THE 1s HYPERFINE SHIFT

The interaction between the atomic electrons and the electric and magnetic moments of the nucleus leads to the hyperfine structure of atomic states, which is well known from optical spectra (Kopfermann, 1958). For the K x rays the splitting is dominated by the contribution from the $1s_{1/2}$ state (see Fig. 8), a contribution which is very much larger than that of the p states.

Even the 1s splittings, however, are not resolvable by x-ray spectroscopy, as they amount to no more than a few percent of the natural line width. Furthermore, in photoionization the net shift of the unresolved line vanishes because the two line components are populated with intensities corresponding to their statistical weights. The first demonstration of 1s hyperfine structure was based on a determination of a minute difference in the natural K-line widths for the pairs of isotopes $^{151,153}\text{Eu}$ and $^{121,123}\text{Sb}$, characterized by large differences between the magnetic moments of the two isotopes (Ryl'nikov *et al.*, 1972).

It was demonstrated by Borchert *et al.*, (1977) that the 1s hyperfine shifts can be observed by using a radioactive x-ray source decaying by electron-capture beta decay (EC). In this situation, the population of the hyperfine levels is no longer statistical and a net shift is measured. In the following two subsections we outline the theoretical and experimental background for this finding.

Fig. 8 Hyperfine splitting of the 1s state caused by a nucleus with spin I and gyromagnetic ratio $g_I = (\mu_I/I)$ (in nuclear magnetons). The atomic parameter for the 1s state a_s (in eV/μ_N) has been calculated with the relativistic Dirac-Fock program of Rosén and Lindgren (1968, 1972). Approximate corrections $[(1-\delta)]$ and $[(1-\epsilon)]$ for nuclear finite size and Bohr-Weisskopf effect have been taken from Kopfermann (1958). The curve allows a fast estimate of the magnetic hyperfine shifts. Note that contrary to normal convention the total angular momentum F arising from the coupling of the nuclear and the atomic angular momentum, I and J , is defined to include only core electrons (here $1s_{1/2}$), the valence electrons having no measurable influence on the hyperfine shifts. The calculated splittings of the atomic p states are at least two orders of magnitude smaller than the 1s splittings and need not concern us here.

5.1 Population of the Hyperfine-Structure Components in EC Beta Decay and Internal Conversion (IC)

For allowed Gamow–Teller beta decay there is no exchange of orbital angular momentum, as the corresponding operator involves only the spin (and isospin) components of leptons and nucleons. If the spin change in the decay is ± 1 , it can be seen from elementary arguments (Fig. 9) that only one of the two hyperfine components can be formed. Another way of realizing this is to consider the total angular momentum F_i of the initial state, defined as the vector sum of the nuclear spin and the angular momentum of the core electron (Fig. 8). Since the only particle leaving the atomic system is a neutrino carrying $1/2$ unit of angular momentum, it can immediately be seen that the final state must have $F_f = F_i \pm 1/2$. Only one of these two components can be realized, however, if the nuclear spin change is unity. For this reason, we refer to this effect as an “ F selection rule” in beta decay. Through the use of standard angular-momentum algebra, the relative population of the two hyperfine states $I_f + 1/2$ and $I_f - 1/2$ can easily be extracted also for the case of $\Delta I = 0$. The result (Borchert *et al.*, 1977) and the corresponding energy shifts are listed in Table I, which shows that for multipolarity zero (Fermi decay) the population ratio is statistical, $(I + 1)/I$, producing no shift, while the intensity ratio for multipolarity one is $I/(I + 1)$ leading to a shift of $-1/2A$. Here A is the magnetic hyperfine-interaction parameter, proportional to the magnetic moment (Fig. 8). The intensity rules of Table I apply also to quasi-allowed first-forbidden transitions (Borchert *et al.*, 1977, 1978a) and to the K excitations following internal conversion of M1 electromagnetic transitions (Egorov *et al.*, 1978).

It is simple to generalize to transitions of multipolarity λ higher than unity. This has been done by Wang *et al.* (1978) and Grushko *et al.* (1981). The latter authors give the following expression for the transition matrix element to the hyperfine state F_f ,

$$H(F_f) = (2F_f + 1)^{1/2} (2j_2 + 1)^{1/2} (-1)^{\lambda} \begin{Bmatrix} I_i & I_f & \lambda \\ 1/2 & j_2 & F_f \end{Bmatrix} \times b_{\kappa}(\tau\lambda).$$

Here j_2 is the angular momentum of the outgoing conversion electron of amplitude b (characterized by the state κ), and τ denotes the type (electric/magnetic) of transition. The total transition probability to the state F_f is proportional to the square of the transition matrix element, summed over κ . Grushko *et al.* (1981), and Fedorov and Ryl'nikov (1979) have pointed out that for mixed transitions an interference term will arise between the different multiplicities. This interference provides a new method for determining the ratio of Fermi to Gamow–Teller matrix elements in beta decay.

The selection rule for $|\Delta I| = 1, \lambda = 1$ (Fig. 9) turns out to be a special case of a more general rule for stretched M λ transitions (that is, with $|I_f - I_i| = \lambda$). We note that the free electron may carry angular momentum $j_2 = \lambda \pm 1/2$ but that in the non-relativistic approximation only one of these occurs for magnetic transitions. [As an example, M2 internal conversion allows electron emission in a $p_{3/2}$ state ($\kappa = -2$) but not in a $p_{1/2}$ state. Both can contribute to an E1 transition.] By evaluating the 6j symbols in the above expression we find that for $I_f - I_i = \pm \lambda$, only the transition to $F_f = I_f \mp 1/2$ is allowed. In the general case, both transitions will occur, but still leading to a non-statistical population.

We may at this point ask to what extent the F selection rules and non-statistical populations discussed above constitute a new effect. It is clear that this cannot be the case from the point of view of beta-decay theory: were it so, then the calculated EC/ β^+ ratios would change drastically and fail to agree with experiment. The usual derivation of EC decay rates in fact involves an averaging that implicitly takes the hyperfine structure into account (see, for example, Wu and Moszkowski, 1965). For experiments involving the polarization of nuclei, photons, or leptons, on the other hand, the selection rules imposed by angular momentum conservation have been discussed by Dolginov (1956, 1958)

Fig. 9 The F selection rule for the population of hyperfine levels is demonstrated here for the case in which the nuclear spin increases by one unit. The initial state has a nuclear spin of $I = 1$ and orbital angular momentum J of zero. The nucleus undergoes beta decay, with capture of an electron, to a state with nuclear spin I . The neutrino carries away half a unit of angular momentum, so that the remaining inner electron can only have its spin antiparallel to the nuclear spin. The hyperfine component with the inner electron spinning parallel to the nucleus is not formed.

and by Bernstein *et al.* (1958), for the case of muonic atoms. One consequence will be the possibility of directional and polarization correlations involving x rays and nuclear γ rays (Rupnik and Crasemann, 1972). A very clear discussion of hyperfine effects in inner-shell processes has been given in a review by Emery (1975). On the other hand, the influence of the non-statistical population of the F states on the energies of x rays does not seem to have been noted previously, as can be seen by comparing the work of Hahn *et al.* (1976) with that of Wang *et al.* (1978).

We note finally that the $1s^{-1}$ lifetimes of 10^{-15} to 10^{-17} s for heavier atoms are much shorter than lifetimes of excited nuclear states, and that the hyperfine shifts may therefore serve to measure magnetic moments of very short-lived nuclear states (Borchert *et al.*, 1977; Egorov *et al.*, 1978; Grushko *et al.*, 1981).

5.2 Experimental Observations of $1s$ Hyperfine Shifts

The $1s$ hyperfine shift has been detected in three experiments. Two of these were carried out under conditions in which other contributions (see Sections 6 and 7) were expected to be small:

i) The first experiment (Borchert *et al.*, 1977) served to compare the energies of K x rays from the EC decays of $^{131,132}\text{Cs}$, for which the main characteristics are given in Fig. 10. The intensity rules of Table I predict a hyperfine shift of 113 meV. The only other expected contribution is the nuclear volume effect, which has been estimated to 13 meV, leading to a total predicted value of 126 meV. This value agrees well with the experimental result for $K\alpha_1$ of 112 ± 11 meV and for $K\beta_1$ of 170 ± 40 meV. The experimental technique eliminates chemical shifts because the two sources were prepared identically by implanting Cs ions into aluminum backings. It also eliminates shake-off and shake-up contributions, which anyway are only 1–2 meV for EC, and which furthermore must cancel in a comparison.

Fig. 10 The difference between the $1s$ hyperfine structure shifts in $^{131,132}(2+)\text{Xe}$ were measured from the K x rays emitted following EC decay of the radioisotopes $^{131,132}\text{Cs}$, with half-lives of 9.7 d and 6.5 d, respectively (Borchert *et al.*, 1977). The relevant parts of the decay schemes (Lederer *et al.*, 1978) are given in the figure, where μ denotes the nuclear magnetic moment in units of μ_N .

Table I

Branching ratios and energy shifts^{a)} of K x rays from allowed or quasi-allowed EC beta decay or from M1 electromagnetic transitions.

Multipole order	ΔI	Relative intensity		Energy shift ^{b)}
		$F = I + 1/2$	$F = I - 1/2$	
1	-1	1	0	$1/2 A \cdot I$
1	0	I	$(I + 1)$	$-1/2 A$
1	1	0	1	$-1/2 A \cdot (I + 1)$
0	0	$(I + 1)$	I	0

^{a)} From Borchert *et al.* (1977).

^{b)} The quantity A is the usual hyperfine interaction constant proportional to the nuclear g factor (see Fig. 8).

Fig. 11 The hyperfine shift associated with K x rays from M4 internal conversion in ^{133}Ba (as a carbonate) was measured by making a comparison with a sample of stable $^{133}\text{BaCO}_3$ excited by photoionization (Grushko *et al.*, 1981). The decay scheme is from Lederer *et al.* (1978).

Fig. 12 The decay scheme (Lederer *et al.*, 1978) of ^{141}Ce , used in the ^{141}Ce – ^{141}Pr hyperfine structure experiment (Egorov *et al.*, 1978).

ii) The experiment on $K\alpha_1$ x rays from internal conversion of a 276-keV M4 transition in ^{133}Ba (Grushko *et al.*, 1981) offers similar advantages. From the information given in Fig. 11 it will be seen that chemical shifts should be absent (identical BaCO_3 samples). The shifts of the lines due to associated atomic excitations are expected to be much bigger than in the previous case (see Sec. 6), of the order of 60 meV, but they should be close to identical for photoionization and internal conversion. The only contribution is thus a 1.3 meV correction for the nuclear-volume effect, after which the experiment determined the increase in energy to 56 ± 8 meV for the $K\alpha_1$ x ray arising from internal conversion. This corresponds to a magnetic moment of $\mu = +0.51 \pm 0.07 \mu_N$ for the $3/2^+$ state. There is, unfortunately, no independent measurement of μ in this case.

iii) In a third experiment (Egorov *et al.*, 1978), x rays from internal conversion of an M1 transition (fed in beta decay) were compared with those from photoionization. The main characteristics are indicated in Fig. 12. Shake-off and shake-up are expected to cancel, leaving, as the main problem, chemical shifts and atomic-structure shifts (see Sec. 4 and 7). The authors solved this problem by noting that the shifts arising from different occupations of the 4f levels are known to be 2.68 times larger for $K\beta_1$ than for $K\alpha_1$. A correction based on this assumption led to a hyperfine shift of 560 ± 50 meV, which corresponds to a magnetic moment of $4.1 \pm 0.4 \mu_N$, in good agreement with the literature value of $4.09 \pm 0.06 \mu_N$. An interesting result is obtained if we correct the raw data for the chemical shifts (Table II). The two measurements give consistent corrected shifts, which must contain a 560 meV contribution from the hyperfine shift, leaving residual shifts of ~ 260 meV and ~ 850 meV for $K\alpha_1$ and $K\beta_1$. The positive sign indicates that the decay product of cerium has about $1/24f$ electron *more* than normal praseodymium, whereas β^- decay without “healing” would be expected to lead to praseodymium with one electron *less*. (See the discussion of the atomic structure effect, Sec. 7 and also Fig. 21.) The interpretation—in agreement with other evidence to be presented later—seems to be that the 4f shell has healed during the lifetime of the 1.85-ns state of ^{141}Pr .

We may conclude that the selection rule effects associated with radioactive decays have offered the first possibility of observing the 1s hyperfine shifts in atoms. It would seem that the theory is sufficiently evident and that the data are sufficiently convincing, so that no great additional effort is required. Still, a few precise experiments under clean conditions [such as (i) and (ii) above] would be most welcome. Calculated hyperfine shifts enter into the analysis of atomic-structure effects, to be discussed in Sec. 7 of this Chapter, and the good agreement obtained for the rare-earth experiments (see Fig. 17) provides additional support for the conclusion given here.

Table II

Shifts (meV) of praseodymium x rays observed in the $^{141}\text{Ce}(\beta^-)$ – ^{141}Pr experiment (Egorov *et al.*, 1978) after correction (Sumbaev, 1978) for chemical shifts of the CeO_2 –Ce, PrO_2 –Pr, Pr_2O_3 –Pr systems

	$K\alpha_1$	$K\beta_1$
PrO_2 reference	790 ± 25	1465 ± 200
Pr_2O_3 reference	870 ± 40	1350 ± 200

6. THE DYNAMIC SHIFT

This Section concerns shifts caused by the excitation mechanism. We shall see that electron-capture beta decay (EC) provides a “clean” way of creating a 1s hole, and that a comparison with x rays from photoionization will, at least in principle, render the shifts due to spectator vacancies observable.

The K x rays may be thought of as arising from a single $1s^{-1}$ excitation, but the real situation is more complicated and must include also excited neutral atoms, double-vacancy excitations, etc. Those excitations that involve the inner shells may shift the x-ray energies considerably and give rise to “satellite lines”, a phenomenon that has been known since the early days of x-ray spectroscopy (see Hedin, 1974). The intensities of satellite lines will depend on the excitation mechanism and energy. Sandström (1957) thus notes that these lines “do not appear in the secondary radiation generated through the irradiation of matter with x rays”. Another extreme limit is reached when atoms are bombarded with heavy ions of high energy. Under these circumstances highly charged intermediate states are formed.

In low-energy nuclear transitions and in photoionization the most easily detectable effects come from an additional vacancy in one of the inner shells. These secondary-ionization effects are weak but resolvable and have attracted the main interest of experimentalists (Freedman, 1974; Walen and Briançon, 1975). The outer-shell ionization is much more abundant, as is known from calculations and from studies of charges of recoil ions from β^- decay (Carlson *et al.*, 1968, and references therein), but the effects tend to be obscured by the natural line width. There are nevertheless many cases where skew or complex line shapes have been observed in the K x rays of light- and medium-weight elements. As an example we quote an experiment by Sauder *et al.* (1977), who studied the Cu $K\alpha_{1,2}$ lines with good resolution. Complex line shapes were found and attributed to $3d^{-1}$ and $3p^{-1}$ spectator vacancies. From a calculated multiplet structure of the double-vacancy peaks combined with the single-vacancy line, all broadened by the instrumental resolution and by the natural width, it was possible to fit the complex peak shape. In units of the *total* $1s^{-1}$ excitations, this fit requires 27% associated $3d^{-1}$ and 2% $3p^{-1}$. There are no calculations of the expected shake-off for copper ($Z = 29$), but the calculations by Nestor *et al.* (1966) predict 15–20% shake-off for the outer shells in argon ($Z = 18$) and krypton ($Z = 36$), so the interpretation by Sauder *et al.* (1977) appears entirely reasonable.

We now turn to the rather limited theoretical and experimental information relating to dynamic energy shifts of K x rays.

6.1 Outer-Shell Shake-Off and its Effect on K x-Ray Energies

A clear and detailed treatment of atomic excitation processes associated with nuclear transitions has been given by Freedman (1974). We recall here a few of the essential features and first consider β^- decay, which for our purposes resembles K-shell photoionization.

It is well known that β^- decay proceeds essentially to the ground state of the daughter *atom*. The gain in binding energy is approximately $\delta B = -\partial E(Z)/\partial Z$, where $E(Z)$ is the total *atomic* energy of the system with atomic number Z . The sudden approximation leads to an expectation value of the atomic excitation energy of only $\langle \epsilon^* \rangle = -\frac{1}{2} \partial^2 E(Z)/\partial Z^2$, which can be demonstrated by the usual techniques for deriving energy-weighted sum rules (Serber and Snyder, 1952). Taking the simplest Thomas–Fermi estimate, $E(Z) = -20.9 \times Z^{7/3}$ eV, we find for gold ($Z = 79$) a total electronic energy $E(Z) = -5.6 \times 10^5$ eV, $\delta B = 1.7 \times 10^4$ eV, and a mean excitation energy $\langle \epsilon^* \rangle = 140$ eV. Thus more than 99% of the atomic energy release is available in the nuclear process. In the words of Freedman (1974), the transition is a “whole-atom one-step process”.

For the EC process it was pointed out already by Primakoff and Porter (1953) that outer-shell excitations are essentially absent in 1s capture in a heavy atom. The reason is that the 1s orbit is very much bunched about the nucleus; consequently, the simultaneous disappearance of a nuclear charge and a 1s electron will affect the potential in the main part of the atom relatively little. (The same argument explains why, in this context, β^- decay and photoionization resemble each other.)

In order to arrive at quantitative estimates of the energy shifts of x rays, it is necessary to turn to detailed atomic models. The usual method for calculating the influence of shake-off processes is to use a cascade picture. In this approximation, the initial process (e.g. 1s photoionization) creates a distribution of vacancies, which in a subsequent series of steps (x-ray emission and Auger cascades) lead to the final (observed) states.

Carlson *et al.* (1968) (see also Nestor *et al.*, 1966) used the sudden approximation to calculate initial vacancy distributions for beta-decay processes and photoionization. The use of the sudden approximation is justified, as the passage time for exiting or produced particles is much shorter than the orbital periods involved. In these calculations, a self-consistent field (Hartree–Fock) calculation was used to obtain the wave functions of the initial and final atomic states. From the single-electron overlap integrals, the excitation probabilities were obtained as unity *minus* the probability that a given state is not excited *minus* a correction for the exclusion of already filled states. Calculations of the excitation probabilities following 1s, 2s, 3s, and 4s electron capture have also been carried out by Crasemann *et al.* (1979), who show that the total excitation probabilities are two orders of magnitude smaller for EC than for PI. This clearly confirms that EC provides an extremely “clean” $1s^{-1}$ excitation, i.e. it has few double-vacancy excitations. As an example, Table III shows the vacancy production probabilities for xenon ($Z = 54$) for PI and EC.

In order to convert the excitation probabilities into contributions to the x-ray energy shift, it is necessary to calculate the shifts in binding energy in the presence of a spectator hole. For accurate calculations this implies the

Table III

Vacancy probabilities and K x-ray energy shifts for Xe ($Z = 54$), $K\alpha_1$

Sub-shell	Vacancy probability $P_i \times 10^4$		$\Delta E(K\alpha_1)^b$ (eV)
	PI ^{a)}	EC ^{a)}	
1s _{1/2}	0.18	0.89	643
2s _{1/2}	3.19	1.89	86
2p _{1/2}	4.18	0.09	105
2p _{3/2}	7.73	0.05	86
3s _{1/2}	8.80	1.36	7.49
3p _{1/2}	13.8	0.10	} 9.82
3p _{3/2}	26.6	0.03	
3d _{3/2}	24.1	0.01	} -0.398
3d _{5/2}	35.4	0.02	
4s _{1/2}	26.0	1.71	1.09
4p _{1/2}	43.7	0.06	} 1.43
4p _{3/2}	86.6	0.02	
4d _{3/2}	187	0.08	} -0.491
4d _{5/2}	287	0.12	
5s _{1/2}	166	2.28	0.059
5p _{1/2}	497	0.02	} 0.089
5p _{3/2}	1229	0.07	

Estimated energy shift for $K\alpha_1$ $(E_{K\alpha_1} = 29779 \text{ eV})$ $\Delta E(K\alpha_1, \text{PI}) = 51 \text{ meV}; \Delta E(K\alpha_1, \text{EC}) = 1.2 \text{ meV}$ ^{a)} From Nestor *et al.* (1966).^{b)} Relativistic self-consistent field calculation as described by Rosén and Lindgren (1968, 1972). Note that only one calculation has been performed for each spin-orbit pair in the outer shells.double difference, for example for $K\alpha_1$ in the presence of a 4f hole,

$$\Delta E(K\alpha_1) = \langle 1s^{-1}4f^{-1} | V | 1s^{-1}4f^{-1} \rangle - \langle (2p_{3/2})^{-1}4f^{-1} | V | (2p_{3/2})^{-1}4f^{-1} \rangle \\ - [\langle 1s^{-1} | V | 1s^{-1} \rangle - \langle (2p_{3/2})^{-1} | V | (2p_{3/2})^{-1} \rangle],$$

where V denotes the total atomic energy. (This is how the atomic structure shifts discussed in Sec. 7 were calculated.) In Table III and in the calculations by Borchert *et al.* (1978b), both based on the self-consistent field techniques of Rosén and Lindgren (1968, 1972), the shifts were approximated by differences in single-electron removal energies for a static Hartree-Fock field, so that only one calculation was carried out for each spectator state. [A previous calculation (Borchert *et al.*, 1978a) had considered only the direct Coulomb terms and had overestimated the shifts by a factor of ~ 2.5 ; see also the discussion of "direct" and "compression" effects, Sec. 4.1.]

The net shifts obtained by combining excitation probabilities and calculated energy shifts are illustrated in Table III and in Figs. 13 and 14. It will be seen that the dynamic shift is expected to increase the energies of K x rays following photoionization by 50–400 meV and to be completely negligible for those following EC. In view of other contributions that are not yet fully understood, it is doubtful whether the differences are observable at our present level of understanding of x rays, although they may have been detected in one experiment, to be discussed in the following.

The discussion of dynamic shifts would not be complete without once again reminding the reader that the cascade picture of inner-shell excitations is an approximation only. A sound quantum-mechanical treatment would have to consider the creation and decay of the inner-shell vacancies as a single process leading to the (experimentally observed) final states. The theory of x-ray line shapes, to which we return in Sec. 8, is of this kind, as are also the calculations by Åberg (1981).

Fig. 13 The gold $K\alpha_1$ line $[(1s_{1/2})^{-1} \rightarrow (2p_{3/2})^{-1}]$ has a natural width $\Gamma = 54$ eV, and it is probably reasonable to assume the same width for the unresolved satellite lines, here characterized by the quantum numbers nlj of the spectator holes. Hyperfine structure of the single-vacancy x ray (heavy line) and of the satellites has not been shown. The dynamic shift results from an asymmetric contribution, hence any accurate calculation must take into account the precise definition of the line position ["the location parameter" (Hansen, 1978)]. The dashed line represents the contour of the complex. (From Borchert *et al.*, 1981b.)

Fig. 14 Dynamic shift in photoionization calculated as in Borchert *et al.* (1978b). The line position is as defined by Hansen (1978) with a measuring interval $2a = 1.2\Gamma$.

Finally, we mention that most experimental and theoretical studies have dealt with shake-off from the $1s$ shell rather than from the outer shells with which we have been concerned here. The $1s$ process clearly serves as an acid test of the theoretical techniques, and for this reason it is relevant to the present paper. References to much work on this subject can be traced through the book edited by Fabian *et al.* (1981) and the paper of Law and Suzuki (1982).

6.2 Experimental Detection of the Dynamic Shift

The first experiment to attempt to detect dynamic effects by comparing electron capture (EC) and photoionization (PI) was carried out by Schnopper (1967), who measured the K x-ray spectra from K capture in radioactive ^{55}Fe and from electron excitation of manganese metal. The spectra turned out to be essentially identical and the precision on the

absolute energies (± 2 eV) was too low to permit conclusions about energy shifts. In a subsequent experiment, Hahn *et al.* (1976) found that for Ta $K\alpha$ the energy for PI exceeded that for EC by about 0.8 eV, but as they believed that shake-off would contribute most strongly for the EC process, they could only understand the sign by postulating a selective multiple shake-off of 4f electrons. It was soon pointed out (Freedman, 1977; Borchert *et al.*, 1977) that there are strong theoretical arguments (cited above as well as in Schnopper's paper) for expecting shake-off to be very weak in the EC process, and that the until then unknown 1s hyperfine shift would increase the effect to 1.2 eV. The quantitative explanation of the data, which meanwhile have been confirmed in several experiments, still remains an interesting problem, which we shall discuss in Sec. 7.4.

A second attempt to detect the contribution to K x-ray energies from shake-off was made by Borchert *et al.*, (1978a), who in a subsequent paper presented a more refined theoretical analysis (1978b). In this experiment, a strong source of 64-h ^{197}Hg was implanted into an aluminum backing, and the energies of the gold x rays were compared with those induced by photoionization in a gold foil. The presence of a 24-h isomer $^{197\text{m}}\text{Hg}$ in the radioactive sample complicated the analysis in several ways (Borchert *et al.*, 1978a), but it was possible to confirm these corrections by repeating the Au $K\alpha_1$ measurement 238 hours after the start of the experiment. The error due to counting statistics amounted to 3×10^{-4} of the natural line width, and the total error was 1.5–2 times bigger when possible systematic errors were taken into account. The results, recalculated to represent the pure 64 h activity, are listed in Table IV. When the hyperfine shift, a small correction for the isomer shift, the shake-off, and the atomic-structure effects are taken into account, the agreement is excellent. This analysis, however, rests heavily on two assumptions, one from nuclear physics and one from chemistry and solid-state physics. The hyperfine shift in the (first-forbidden, “quasi-allowed”) EC decay is $-6-392(1 + y^2)^{-1}$ meV, where y^2 is the intensity ratio of multiple order zero to multiple order one. From nuclear-structure arguments it seems reasonable to assume $y^2 = 0.05$; even though this correction is small, it would be desirable to have a measured value.

Table IV
Energy shifts^{a)} of gold K x rays in meV

Line	Calculated value			Experiment
	Shake-off ^{b)}	“6s” ^{b)}	Total ^{c)}	
$K\alpha_1$	70	83	543	568 ± 36
$K\alpha_2$	70	94	554	567 ± 46
$K\beta_1$	124	95	609	620 ± 50

^{a)} Defined as the energy for x rays from photoionization of gold *minus* the energy for x rays from EC of 64-h ^{197}Hg . The experimental data (Borchert *et al.*, 1978a,b) are presented here without contributions from the 23.8-h isomer and from tails of neighbouring mercury x rays.

^{b)} The energy shifts due to shake-off and valence electrons were calculated by the techniques discussed in Secs. 6.1 and 7.1.

^{c)} The total theoretical shifts include a 378-meV contribution from magnetic hyperfine structure and a 12-meV isomer shift.

The second and more serious problem concerns the correction for the atomic-structure shift (Sec. 7). It was assumed in the experiment that in metallic samples the elements gold and mercury (here implanted into aluminum) had electronic structures that could be approximated by the free-atom configurations, 6s and 6s², outside a platinum core. There is now evidence that such assumptions fail entirely for the 5d elements (Fig. 19), and there is no *a priori* reason why we should fare better in the Au–Hg case and in the rare earths (Figs. 16 and 17), as seems to be the case. For the Au–Hg case, the agreement is quantitative: the weighted difference between theory and experiment for all lines is 16 ± 26 meV, but 104 ± 26 meV if the shake-off shift is not included.

In summary we can conclude that the experimental evidence is consistent with a small shake-off shift, of the magnitude shown in Fig. 14. Further experimental work is clearly desirable.

7. THE ATOMIC-STRUCTURE SHIFT FOR TRANSITIONS WITH $\Delta Z = 1$

The process of nuclear electron-capture (EC) transforms an element with atomic number Z into one with atomic number $Z - 1$. The associated x rays are therefore emitted from an atom containing one electron “too many”, in which

Fig. 15 Atomic structure shifts ($E_{PI} - E_{EC}$) for the K-series x rays ($np \rightarrow 1s$) as a function of the quantum number n . Each pair of atoms is characterized by the quantum numbers (nl) of the orbital filling at this point and by the atomic number Z of the daughter. These calculations have been carried out with Desclaux's (1975) Dirac-Fock computer program, where the energy differences are between total energies, so that full relaxation is included in the calculation. Note that the shift displayed here is the *negative* of that for the addition of the electron indicated.

the outer shells have the electronic structure of the next-heavier element. By comparing the x-ray energies with those obtained from processes with $\Delta Z = 0$ (photoionization, internal conversion), it is possible to observe energy shifts that reflect the difference in atomic structure of two neighbouring elements. For this reason, we refer to a shift caused by this mechanism as an atomic-structure shift (Borchert *et al.*, 1978b).

It is clear from the discussion in Sec. 6 that the outer shells are temporarily in a stable state for an atom formed in EC decay. When the same atom is formed in photoionization (PI), it will be able to bind one more electron, but the lifetime of a $1s$ hole (10^{-15} – 10^{-17} s for one of the heavier atoms) seems somewhat short for a rearrangement to occur. We may therefore expect the atomic-structure shift (PI – EC) to provide a “snapshot” of the two structures. For the case of β^- decay followed by K internal conversion, the time available for rearrangements is given by the nuclear lifetime, and the observed shift may depend upon the lifetime of the intermediate state. Such effects very likely play a role in the $^{141}\text{Ce}(\beta^-)$ experiment discussed in Sec. 5.2 (iii).

It is possible to calculate the influence of different atomic structures by the self-consistent-field method used for treating the dynamic shift (Sec. 6). Again, it is essential to calculate the shifts as a double difference between the total energies of the four states involved, thus taking into account the full relaxation. To illustrate the expected pattern of atomic-structure shifts, we show in Fig. 15 the results obtained for pairs of elements in which the occupation of the indicated orbital differs by unity. It is characteristic that addition of a typical valence electron (s or p) gives rise to a small negative shift of $K\alpha_1$, $K\beta_1$, $K\beta_2$ whereas the d and, even more so, the f orbitals lead to large positive*) shifts corresponding to the compression effect (Table III, Sec. 4). Experiments on transition elements therefore should offer the best possibilities for observing the atomic-structure shift.

The atomic-structure shift is not identical with the chemical shift discussed in Sec. 4: chemical shifts are observed between *different chemical states of the same element*, while the atomic-structure shift is observed between *different elements in the same chemical state*, usually the metallic state. The difference is well illustrated by Figs. 7 and 17, which show that the $Z, Z-1$ calculation describes the atomic-structure shift quantitatively while the corresponding free-atom-ion estimate of the chemical shift is an overestimate; a more accurate calculation would have to take the nature of the chemical bond into account.

We now discuss the experimental evidence on atomic-structure shifts, grouped according to the atomic orbitals. The atomic-structure shifts used in this section are based on single electron configurations calculated in a Dirac-Fock computer program developed by Desclaux (1975). Previous results (Borchert *et al.*, 1978b; Hansen *et al.*, 1981), which were based on calculations developed by Rosén and Lindgren (1968, 1972) agree to within typically 0.1 eV so that the conclusions are not sensitive to details of the atomic model.

*) The sign conventions for the x-ray energy shifts may lead to confusion, especially since the definition of the signs is not specified in some papers. We have, here and in previous papers, presented the experimental data as “energy in photoionization *minus* energy in EC” (often abbreviated PI – EC). The atomic-structure shift is thus the negative of the shift due to the addition of an extra electron. In the calculation of the dynamic shift, we are dealing with vacancies (see Table III and Fig. 13). Consequently, the 4f shifts appear negative throughout this paper.

7.1 The 6s Elements

The only data until now are for the pair ^{197}Au (PI), ^{197}Hg (EC) discussed in subsection 6.2. The results of Table IV are presented graphically in Fig. 16, which shows excellent agreement with a calculation for which the underlying assumption is that metallic Au and Hg samples can be described by free-atom calculations (cf. Sec. 6.2). The net contribution of the atomic-structure shift is, however, too small in this case to furnish a sensitive test of the theory.

7.2 The 4f Elements

The rare-earth elements furnish an ideal testing ground for the atomic-structure shift, not only because the 4f electrons give large shifts (Fig. 15), but also because these elements (excluding Eu and Yb) have nearly identical chemical properties. Thus, holmium and erbium (Fig. 17) both crystallize in an *hcp* lattice and differ by less than 1% in the lattice constants. There are therefore strong reasons for believing that chemical shifts should be absent. The good overall agreement obtained between theory and experiment is a striking verification of the existence of an atomic-structure shift.

Fig. 16 The energy shifts $E(\text{PI}, np \rightarrow 1s) - E(\text{EC}, np \rightarrow 1s)$, with $n = 2, 3$ for the pair $^{197}\text{Au}(\text{PI})$ - $^{197}\text{Hg}(\text{EC})$. The experimental results of Borchert *et al.* (1978a, 1978b) are denoted by dots, together with their total uncertainties. The horizontal line corresponds to the sum of isomer shift (12 meV) and hyperfine shift (378 meV). It represents the nuclear contribution. The total shifts, given by the dashed line, consist of isomer shift, hyperfine shift, dynamic shift, and atomic-structure shift due to an additional 6s electron for the EC case. These data were also presented as Table IV. Note the offset zero of the y axis.

Fig. 17 The energy shifts $E(\text{PI}, np \rightarrow 1s) - E(\text{EC}, np \rightarrow 1s)$ for x rays from metallic samples of rare-earth elements ($n = 2$ to $n = 5$). The left-hand side shows data for the pair $^{159}\text{Tb}(\text{PI})$ - $^{159}\text{Dy}(\text{EC})$ ^{159}Tb (Hansen *et al.*, 1981), and the right-hand side shows data for the pair $^{165}\text{Ho}(\text{PI})$ - $^{165}\text{Er}(\text{EC})$ ^{165}Ho (Borchert *et al.*, 1978b). The experimental results are represented by dots together with the corresponding total uncertainties. In cases where the error bar is not shown, it is smaller than the diameter of the dot. The horizontal line gives the calculated hyperfine contribution to the shifts (Sec. 4). Relativistic atomic calculations have been carried out by the method of Desclaux (1975). The dot-dashed lines represent the total theoretical shifts for the assumed configuration "Xe core" $6s^2 5d(4f_{7/2})^9(4f_{5/2})^2$ for terbium, and the configurations $(4f_{7/2})^3$, $(4f_{7/2})^4$, $(4f_{7/2})^5$ for dysprosium, holmium, and erbium, respectively. These are the expected electronic configurations for these (trivalent) metals. The dashed lines are under the assumption of divalent metals, an assumption that is ruled out by simple arguments from solid-state physics (Johansson, 1975).

It is interesting to perform the calculation assuming other configurations than $6s^25d4f^m$, which is known to be the right one for the four elements involved here (see Johansson, 1975). If instead we assume $6s^24f^{m+1}$, corresponding to the divalent structure of Eu and Yb metals, we get poorer agreement (Fig. 17), and versions involving either a change in the number of 5d electrons or a change of two 4f electrons can be completely excluded.

In order to test whether the results are very sensitive to the chemical environment, the Ho–Er experiment was repeated in part with $^{165}\text{Er}(\text{EC})$ implanted in Al metal. The results (for $K\alpha_1$ and $K\beta_1$) were unchanged within the experimental errors (Borchert *et al.*, 1978b).

In two other experiments, energies from photoionization and beta decay of rare-earth elements were compared. The experiment on β^- decay of ^{141}Ce was discussed in Sec. 5.2 (Egorov *et al.*, 1978); in the other experiment, Eu K x rays from photoionization of Eu_2O_3 were compared with those from the EC decay of ^{153}Gd (Wang *et al.*, 1978). In both cases, however, the shifts contain also contributions from internal conversion and from (possible) effects of nuclear lifetimes. The latter problem is discussed in Sec. 9.

It is interesting to compare the shift pattern due to the atomic-structure effect with that caused by chemical binding (Sec. 4). The physical difference is evident: the atomic-structure shift in the rare earths arises from the fact that in the EC process there is exactly one electron more which is in a pure and localized state. On the other hand, the chemical shift is caused by the involvement of 4f electrons in a chemical bond. Consequently, the amount of “removal” of the 4f electron depends sensitively on the ionicity of the bond, and the theoretical value from free-atom-ion calculations is reached only as a limit (Fig. 7).

7.3 The 4d Elements

The only case studied involved metallic samples of $^{103}\text{Rh}(\text{PI})$ – $^{103}\text{Pd}(\text{EC})$ (Hansen *et al.*, 1981). The shifts do not agree with calculations based on simple assumptions about the electronic structure of the two elements (Fig. 18). The situation seems to be similar to that of the 5d elements.

Fig. 18 The energy shifts $E(\text{PI}, np \rightarrow 1s) - E(\text{EC}, np \rightarrow 1s)$ as a function of n ($n = 2-4$) for the pair $^{103}\text{Rh}(\text{PI})$ – $^{103}\text{Pd}(\text{EC})$. The experimental results of Hansen *et al.* (1981) are denoted by dots with the corresponding error bars. Again the horizontal line represents the calculated hyperfine shift contribution of 278 meV. The three curves shown correspond to the calculated total shift for three different configurations. ^{103}Rh is assumed to have the configuration “Kr core” $(4d_{3/2})^4, (4d_{5/2})^4, (5s_{1/2})^1$. The configuration of ^{103}Pd is taken as: ... $(4d_{3/2})^5, (5s_{1/2})^1$; ... $(4d_{3/2})^6$; R ... $(4d_{3/2})^4, (5s_{1/2})^2$, where the second configuration is the one normally assumed for the Pd atom.

7.4 The 5d Elements

A more extensive set of data for the atomic structure effect is available for elements in which the 5d shell is being filled. The first measurements were performed with oxide sources on the strong lines in the pair $^{181}\text{Ta}(\text{PI})$ – $^{181}\text{W}(\text{EC})$ (Hahn *et al.*, 1976; Wang *et al.*, 1978). A complete set of data with metallic sources was obtained for the pairs $^{181}\text{Ta}(\text{PI})$ – $^{181}\text{W}(\text{EC})$, $^{185}\text{Re}(\text{PI})$ – $^{185}\text{Os}(\text{EC})$, and $^{189}\text{Os}(\text{PI})$ – $^{189}\text{Ir}(\text{EC})$ (Borchert *et al.*, 1980b; Hansen *et al.*, 1981).

In the case of Ta and W the chemical shift between metal and oxide is known (Sumbaev, 1976). The common lines of the different Ta–W experiments can therefore be compared directly, and they agree within the quoted errors. The experimental data for these three pairs together with the results of the corresponding shift calculations for the atomic-structure effect of an additional 5d electron are shown in Fig. 19.

Fig. 19 The energy shifts $E(PI, np \rightarrow 1s) - E(EC, np \rightarrow 1s)$ in the 5d elements for x-ray transitions as a function of n . The experimental results for three different pairs of elements (Hansen *et al.*, 1981) are given by the dots with corresponding error bars. The solid lines denote the calculated hyperfine shift, whereas the dotted lines correspond to the total shifts including the atomic structure shift. The configuration for Hf is "Yb core" $5d^4$ and similarly for the other elements. The disagreement is general; note especially the drastic jump of the K α shift.

Fig. 20 The differences of the experimental and the calculated total shifts of the x-ray transition energies in the 5d elements. For each measured pair of elements the difference $\Delta E_{\text{exp}} - \Delta E_{\text{calc}}$ is shown as a function of the occupation number ρ of the 5d shell. Note that the scale of the shift differences varies. It seems that the shift differences from the L, M, and N shell follow a linear trend with ρ .

It is interesting to note that in these cases the calculation reproduces neither the pattern nor the absolute values of the shifts. The calculation predicts a smooth behaviour with an amplitude of about ± 0.5 eV. Even for the transitions of the innermost shells, the experimental data differ from the theoretical predictions by more than 1.5 eV, whereas the shifts of the K α transitions amount to more than 4 eV.

A systematic compilation of the results is provided in Fig. 20, which shows the differences between experimental and calculated shifts as a function of the occupation number of the 5d shell. The different scales are denoted by the corresponding transitions. It is striking that all transitions from the L, M, N shells show a linear trend and change sign in the vicinity of osmium.

By contrast, the difference between the calculated and the experimental shifts for the K α transitions is more or less constant but as large as 4 eV. There is no quantitative explanation for this behaviour in the 5d elements. It is

striking to note, however, that the change of sign for the differences coincides with the minimum of the corresponding atomic radii and the minimum of the 5d and 6s binding energies (Huang *et al.*, 1976). There might be an indication that one would have to take into account the influence of the metallic lattice (Wang *et al.*, 1978a,b; Borchert *et al.*, 1978b; Hansen *et al.*, 1981). (This interpretation is clearly related to the subject of core-level shifts, referred to in Sec. 4.2.) The interpretation of the anomalous W-Ta shifts as a solid-state effect finds support in an experiment in which the energies of Ta $K\alpha_1$ x rays from a 2% alloy of tantalum in tungsten (W) were compared with those of pure tantalum metal (Wang, 1979). The shift of -0.46 ± 0.14 eV is in the right direction but insufficient to explain the full effect.

8. OTHER CONTRIBUTIONS

Additional small contributions to the x-ray energies are considered in this section. These contributions have not been studied experimentally and, except for special cases, it is safe to neglect them.

8.1 Deviations from the Breit-Wigner Single-Level Line Shape

So far in the present paper, the modifications of x-ray line shapes have had their origin in unresolved multiplet structures such as hyperfine structure (Sec. 5) and satellite lines (Sec. 6). It has been assumed that the basic line shape could be described by the Breit-Wigner formula, which is a good approximation as the natural width of a K x ray is at most 10^{-3} of the energy. At a certain level of precision it becomes necessary, however, to consider other contributions to the energy arising from energy conservation (the tails of the line cannot extend to infinity) and non-resonant terms. We now examine these.

We are aided in this task by the existence of a complete theory of the line shape of x rays following EC beta decay. This theory (developed by Glauber and Martin, 1956; Martin and Glauber, 1958) predicts that E1 internal bremsstrahlung becomes extremely intense at low energies, where it merges continuously with the characteristic x rays. The theory has been extended to cover the x-ray region by De Rújula (1981), who gives approximate expressions, which have been used in the following.

As we shall now be dealing with asymmetric line profiles, it is useful to begin by considering the definition of the line position, or "location parameter" in statistical terminology. Measuring the photon energy k and natural width Γ of the line in units of the transition energy, we need only to consider the profile

$$G(x) = (1 + 2ax)/(x^2 + \gamma^2/4), \quad (8.1)$$

which is sufficiently general for our purposes, and where

$$x = k/E[K_x] - 1. \quad (8.2)$$

The resulting shift may be written

$$\Delta x = C\gamma^2,$$

where the constant C depends on the definition of the location parameter. Taking this to be the mode [i.e. the maximum with $dG(x)/dx = 0$], we have $C = 0.25$. A more useful definition is to truncate the line and to define the location parameter as the center of gravity after a bias correction (Hansen, 1978). With this definition and a truncation interval of approximately 1.2γ , we obtain $C \cong 0.4$.

For allowed x rays, the transition probability to a given final state nlf may be written (De Rújula, 1981)

$$d\omega[nlf]/dk = \text{const } |Q_{np}|^2 \phi(k), \quad (8.3)$$

where the resonant structure is contained in the matrix element Q_{np} , and where the phase-space factor divided by the photon energy k is

$$\phi(k) = (Q - B[nlf] - k)^2 k, \quad (8.4)$$

with Q denoting the energy available and $B[nlf]$ the binding energy of the electron in the daughter atom. As the shift arises from contributions inside the natural width $\Gamma(K_x)$ of the x ray, it is sufficient to consider linear terms in the variable x (Eq. 8.2) and we find the contribution from ϕ

$$\Delta E_{EC,1} \cong 0.4 \Gamma^2 [K_x] \{1/2/E[K_x] - 1/(Q - B[1s_{1/2}])\}, \quad (8.5)$$

which is small in almost all cases. For the decay of ^{235}Np ($Q = 123.0$ keV, $B[1s_{1/2}] = 115.6$ keV, and $\Gamma = 110$ eV) we find a resulting shift of -0.63 eV.

The matrix element Q_{np} contains a sum over intermediate states. At the position of the K x ray the non-resonant contribution may be approximated by a constant β so that the line shape is

$$G_1(x) = |(x + i/2\gamma)^{-1} + \beta|^2, \quad (8.6)$$

which to the lowest order in x gives the shift

$$\Delta E_{EC,2} \cong 0.4\beta\Gamma^2[K_x]/E[K_x]. \quad (8.7)$$

With β calculated from the expressions given by De Rújula (1981), the shifts for uranium x rays are -0.005 eV, $+0.009$ eV, and -0.064 eV for $K\alpha_1$, $K\beta_1$, and $K\beta_2$, respectively. Similar interference effects between resonant and non-resonant contributions have been studied for the $2s2p$ autoionizing state of helium ("Fano resonances", see Hedin, 1974).

For photoionization there is to our knowledge no equivalent to the Glauber–Martin theory. It is easy to calculate the phase-space contribution in this case for an incident photon energy k_0 and with an outgoing free electron, and one finds when Coulomb interactions with the outgoing electron are included a constant shift

$$\Delta E_{PI,1} \cong 0.4\Gamma^2[K_x]^{1/2}/E[K_x]. \quad (8.8)$$

The constant term vanishes in experiments that compare EC and PI. The absence (to lowest order) of an energy-dependent term is reassuring for the x-ray experimentalist, since the energies he measures will not depend appreciably on the choice of photo-excitation source. This, of course, no longer holds when the excitation line coincides with the K edge, a case that has been studied theoretically and experimentally by Grushko *et al.* (1978).

The contribution from non-resonant terms would have to include also the d states. This effect has not been evaluated, but it is tempting to speculate that it could be more important here than in EC decay.

8.2 The Coupling of Atomic and Nuclear Excitations

The energy shifts arising from the finite (or rather non-zero) nuclear size were discussed in Sec. 3. The corresponding off-diagonal contribution will lead to mixing of atomic and nuclear excitations and to small energy shifts. Such phenomena are well-known in muonic and pionic atoms, but they are essentially negligible in electronic atoms.

It was pointed out by Morita (1973) that such processes might become observable by resonant enhancement in cases where a nuclear excited level with the right quantum numbers coincides in energy with an x-ray transition. In a first experiment of this kind (Otozai *et al.*, 1978) a nuclear isomer ^{189m}Os was formed in bombardments with 70–100 keV electrons. The production threshold agreed with the Os K binding energy. The process, referred to by the authors as "nuclear excitation by electron transition" (NEET), can be viewed as inverse internal conversion. In the ^{189}Os case the probability of nuclear excitation of 1.2×10^{-7} corresponds to a coupling matrix element of 0.89 eV. The calculated shift for this case would be only 0.35 meV.

In a second experiment on ^{237}Np a marginal effect was observed in direct photon counting for an $E1-K\alpha_1$ pair (Saito *et al.*, 1980). The deduced off-diagonal matrix element was 26 ± 4 eV, leading to a calculated shift in this case of 0.36 eV. Effects of this kind could thus accidentally play a role for x-ray energies.

9. CONCLUDING REMARKS

Although considerable progress has been made in our understanding of the mechanisms for energy shifts in K x rays, there still are points that seem to need further clarification, and there are many possibilities for applications.

The dynamic shift has not been well established, and it would be interesting to have more precise measurements for checking the expectations of Fig. 14. The atomic-structure shifts for the 4d and 5d elements (Figs. 18–20) present a major puzzle; it is not at all clear where the additional shifts have their origin. If, as most authors are inclined to believe (Sec. 7.4), the effect originates in an incomplete description of the electronic structure, then the mechanism could involve either the free atom, or, perhaps most likely, the electronic structure of the solid. In the latter case the problem would be intimately linked to the core-level binding-energy shifts of metals. More experiments are clearly needed.

We have here and there touched on applications of the effects discussed in this Chapter, and in Sec. 5.2 we have cited the first determinations of nuclear magnetic moments by a new technique. As pointed out in the previous paragraph, the atomic-structure shift leads to investigations of the electronic structure of atoms and solids. A further development (Fig. 21) could be the determination of the healing time of certain electronic defects.

Fig. 21 Approximately 36% of the x rays emitted from the EC decay of ^{153}Gd originate in internal conversion. The nuclear intermediate states (in ^{153}Eu) have half-lives of 10^{-9} – 10^{-10} s. The analysis shown here aims at detecting whether the Gd atom has had time to shed the surplus 4f electron (to “heal”) before the x rays from conversion are emitted. The experimental data (Wang *et al.*, 1978b) compare PI and EC from trioxides of the two elements, so that there is no chemical shift. The upper line indicates the contribution from the hyperfine shift and the isotope shift. In addition to the dynamic shift, the theoretical estimates include either an atomic-structure shift only for the x rays associated with EC (dashed line), or the same atomic-structure shift is assumed for all x rays (full drawn line). The atomic-structure shift was calculated according to Rosén and Lindgren (1968, 1972). The experimental indication thus is that only the x rays from EC are shifted, so that the Gd structure is lost in no more than 10^{-9} – 10^{-10} s (Wang *et al.*, 1978a, 1978b). The ^{141}Co experiment discussed in Sec. 5.2 (iii) and Table II suggests a similar conclusion.

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