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MUON DIFFUSION IN Cu BELOW 2 K

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ABSTRACT.

We have performed transverse field μ SR experiments on several different samples of copper in the temperature range below 2 K, including isotope separated Cu and impurity doped polycrystalline Cu.

We do not observe any strong effect of the isotope composition of the samples. A ^{63}Cu and a natural Cu sample of identical purity both yield $0.16 \mu\text{s}^{-1}$ for the low-temperature plateau, while an increased linewidth in the ^{65}Cu case may be related to the strong effects of Fe impurities.

Careful transverse field measurements on large single crystals at 0.08 K reveal non-Gaussian lineshapes in accordance with the picture of diffusing muons at this temperature. This allows us to reject several of the existing models for muon behaviour in copper below 2 K.

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INTRODUCTION.

Copper is one of the metals most studied by the μ SR technique; and for a long time it appeared to be a very well understood system. The early measurements showed clearly that the muons are essentially immobile below 100 K, with motional narrowing taking place above 100 K up to room temperature [1, 2]. The transverse depolarization rate (or linewidth) remained almost constant below 100 K, and its value ($0.25\text{--}0.27\ \mu\text{s}^{-1}$) was not far away from that expected for muons localized and immobile at interstitial sites in the lattice.

The parameters describing the motional narrowing region showed that the apparent activation energy for muon diffusion is rather low and that the prefactor is far below what could be possible with classical diffusion processes. These results have been perfectly well explained with the quantum theories of diffusion for small polarons [3, 4].

The measurements on single crystal copper at 20 K and 80 K showed that the muons occupy octahedral interstitial sites [5] and that magnetic field strengths of about 1000 G are needed to overcome the electric field gradient created by the muons on the surrounding copper atoms [6]. Since the agreement with theory was very good both for the field dependence and the diffusion behaviour, and furthermore all existing measurements gave approximately the same results, the case appeared to be complete.

Renewed interest arose when it was found [7] that the linewidth for polycrystalline copper drops from $\sim 0.25\ \mu\text{s}^{-1}$ to $\sim 0.16\ \mu\text{s}^{-1}$ when the temperature is lowered below 2 K. The decrease is in fact gradually setting in below ~ 20 K, and below 0.5 K the linewidth seems to have reached a temperature-independent value. Single-crystal measurements [8] also confirmed the reduction of the linewidth, and it was found that the muon site is still dominantly octahedral at 0.1 K.

Several different models have been proposed for the low-temperature region in Cu, since the linewidth reduction could be either static (an extended muon wave function) or dynamic (slowly diffusing muons). Chappert et al [8] assumed mobile muons, diffusing by the one-phonon process at low

temperatures. Above 0.5 K the mobility starts to increase with increasing temperature, which was interpreted as leading to trapping at residual impurities above 2 K. Clawson et al [9] were made zero-field μ SR-experiment down to 0.5 K, and these data are interpreted as moving muons, but with increasing mobility as the temperature is lowered. This inverted temperature dependence should point to coherent diffusion of the muons.

Recently, Stoneham put forward the idea that muons may not always localize immediately at their stable self-trapped ground state positions but may rather form long-lived meta-stable states, which during the lifetime of the muon may not decay into the ground state [10]. Such a process should be of particular importance if more than one energetically low-lying interstitial site exists. Under these circumstances a large muon fraction may first localize at the energetically less favourable meta-stable interstitial site and may only slowly decay into the ground state. Seeger has developed this idea in detail for the case of Cu, proposing that initially the muon localizes with equal probability at tetrahedral (T) and octahedral (O) sites [11]. The T-sites have a shallow potential and therefore a somewhat more extended muon wave function. The plateau region below 0.5 K is then explained as a configuration which is static over the muon lifetime and where the muons are partly occupying O sites (in a localized wave function) and T-sites (extended wave function). The resulting reduced linewidth is in such a case expected to be of static nature. With increasing temperature the muons start to decay into the octahedral holes and the linewidth increases. Above about 10 K this decay is fast with respect to the time window of the μ SR experiment and the muons are observed only at the O-sites.

It is surprising that the damping rate should change at low temperatures in copper, but it is also surprising that there is a damping rate at all in this metal. It has emerged gradually that many metals (Al, Nb, V and others) show an intrinsically very fast muon diffusion, and that the large linewidths originally observed in these metals were due to trapping at impurities [13] (or other imperfections). Since Cu now appears as an exception one may rather ask why the diffusion is (comparatively) slow even in exceedingly pure samples of this metal.

One explanation of the very fast diffusion of muons in metals like Al

and Nb at lower temperatures is that a coherent propagation mode or band-state for the muon develops. These coherent tunnelling processes can be limited by scattering against phonons or electrons, or by disorder created by strains around impurities in non-pure samples which shift the energy levels and destroy the coherence. Impurity doping in the order of 10-100 ppm has, for instance, a very strong influence on the muon diffusion in Al [12], while the purest Al-samples show very fast muon diffusion at all temperatures studied.

One property of natural copper which may distinguish it from e.g. Al and Nb is the question of isotopic composition. These two metals, which show fast muon diffusion if sufficiently pure, consist naturally of only one isotope. Natural Cu on the other hand contains 69% ^{63}Cu and 31% ^{65}Cu . This mixture would obviously reduce the homogeneity of the lattice, and might bring about a disorder large enough to destroy the conditions for coherent motion of the muons [14].

In this paper we report on various measurements on copper samples, including isotope separated ^{63}Cu and ^{65}Cu . The measurements have mainly been concentrated to the low-temperature region (below 10K), and were initially aimed at checking the effects of the isotopic composition. However since the chemical impurity content is of fundamental importance we have also compared a few copper samples of different impurity doping. Finally the question of diffusion or delayed localization at the lowest temperatures was studied by transverse field lineshape studies on large single-crystal samples of natural copper (i.e. time-differential analysis of the damping).

EXPERIMENTAL.

The μSR measurements reported here were performed at CERN, Geneva, using polarized muon beams from pions decaying in flight. The details of the set-ups have been described elsewhere [12]. Most of the data presented here were obtained with a dilution refrigerator, which covered the range from ~ 0.05 K up to ~ 10 K (higher temperatures are possible, but with less accuracy). Above 2 K a ^4He cryostat was normally used, and a certain overlap of the temperature ranges is possible. The temperatures were determined from calibrated germanium, carbon and platinum resistors.

All the measurements were done in transverse magnetic fields, ranging from 80 to 1500 G. The data were normally evaluated in terms of a Gaussian decay of the muon polarization, $P(t) = P(0)\exp(-\sigma^2 t^2)$, where σ was used as a fitting parameter characterizing the depolarization rate even in the cases where the lineshape deviates from the Gaussian. Corrections were made for the fraction of muons stopping in the sample holder and cryostat walls [12]. This procedure, was not necessary in the case of the big single crystal samples, where the fraction of precessing muons outside the samples was negligible.

For the single crystal samples, detailed comparisons were made with the different proposed models of diffusion or delayed self-trapping. The data analysis was therefore carried out with non-standard methods, described in the Results section.

SAMPLE PREPARATION.

In this section the preparation of the samples made from isotopic pure copper, from iron and silicon doped copper and from poly- and mono-crystalline high-purity copper will be described. As copper batches from three different origins were used for this program, a meaningful interpretation of the results will only be possible if the purity of the samples is well characterized. The most appropriate technique is spark-source mass-spectrometry [15]. Nevertheless one should keep in mind that only information on the mean impurity concentration is obtained, and the method does not tell whether the impurities are dissolved in the bulk or segregated in precipitates or at structural defects. When impurities are present at the ppm level in copper, it can be deduced from residual resistivity measurements [16], or directly be observed by secondary-ion mass-spectrometry [17], that the latter situation is usually valid.

Fifty grams of isotope separated copper (^{63}Cu and ^{65}Cu) were obtained from Techsnabexport, USSR. The analysis by the producer for these batches are given in Table 1. The high impurity level made this material unacceptable for the planned experiments. Therefore it had to be purified by electrolysis and vacuum fusion with the aim to depress the impurity content below the 10 ppm mark.

For the electrolysis the copper was dissolved in HNO_3 , in a beaker of fused silica, and deposited on a titanium strip. The Winkler anode was made from platinum. During the electrolysis the cell voltage was kept at 2 V and the pH of the solution at 0.5. For each batch two fractions of approximately thirty and twenty grams were collected, the first one being the high-purity one. The vacuum fusion was performed in a flat crucible made from high-purity graphite at a pressure of 10^{-5} Torr. For comparison a piece of high-purity natural copper (grade A-58 from ASARCO, USA) was also melted. The ingots had a diameter of 20 mm and exhibited a coarse grained structure with typical grain diameters of 5 mm. The results (in at. ppm) of the spark-source mass-spectroscopy analysis shown in Table 1 represent the mean value of six analyses for each sample. The relative standard deviation for the isotope determination is 4% and for the impurities usually less than 30%. The concentration of non-listed elements is less than one ppm. The isotope enrichment factors appear to be higher than the ones given by the producers. The purification goal was reached, although the purification was more efficient for the ^{63}Cu isotope. During the electrolysis a contamination with platinum occurs. The values for Al, S, Cl, K, Ca, Ag represent upper limits, because large quantities of samples containing these elements were analyzed before the copper samples.

The purity of the ^{63}Cu isotope is comparable to that of the natural high-purity Cu A-58. Because of the low solubility of carbon and sulfur in copper [18], it can be fairly safely assumed that these impurities either are present as graphite and Cu_2S inclusions, or are segregated at dislocations [19]. The most important impurities in the ^{65}Cu isotope are Fe, Pt and Al. A major fraction of these impurities will be dissolved in the bulk because they are soluble to some extent in copper [18] and the oxygen level is too low to bind Fe and Al by internal oxidation [17].

To prepare the Fe and Si doped copper samples, master alloys were made by induction melting high-purity copper (A-58 from ASARCO, USA) and 1 w.% of high-purity iron and silicon in alumina crucibles. The atmosphere consisted of high-purity argon at 1 bar. After solidification, the alloys were annealed for several hours at 1200 K. The dilute alloys were obtained by melting under the same conditions high-purity copper and adequate

amounts of the two master alloys. The nominal concentrations were 100 at. ppm for both dopants. The ingots were rolled to a thickness of 0.5 cm and annealed in vacuum at 1270 K. To minimize internal oxidation, the plates were put on supports made of high-purity graphite. The iron and silicon content was checked by ICP-optical emission spectroscopy (courtesy G. Wolff, ZCH, KFA Jülich). The results were 95 ± 0.4 at ppm Fe and 109 ± 2 at ppm Si, which are the mean values of 6 and 9 determinations, respectively, and are in good agreement with the nominal concentrations.

For the growth of single crystals, high-purity electrolytic copper from Kabel- and Metallwerke, FRG, was used. A mass-spectrometry analysis of a vacuum remelted test-piece is given in Table 1. It appears that this copper is the purest one used in the present program. The residual resistivity ratio of the test-piece was 7350. This shows that most of the impurities must be segregated because only one at. ppm of dissolved Fe could be sufficient to decrease the residual resistivity ratio to 1000.

First a blank ($\emptyset$: 6.5 cm, length: 18 cm) was made by vacuum induction melting of pieces of the cathode in a high-purity graphite crucible. Then a (110)-oriented crystal was grown in vacuum by the Bridgman technique. Two cylindrical pieces ($\emptyset$: 3.2 cm, length: 6.5 cm) with (100)- and (111)-axes were machined by spark-erosion from the crystal by using a tube electrode. The mean full width of the rocking-curves at half maximum as measured by γ -diffractometry was approximately $10'$.

RESULTS.

The isotope separated ^{63}Cu sample was first measured as it arrived, before purification. It then contained ~ 400 ppm of chemical impurities, including 147 ppm Fe. The μSR linewidth was measured down to 0.07 K temperature and although the damping rate σ drops from $0.24 \mu\text{s}^{-1}$ at 80 K to $\sim 0.20 \mu\text{s}^{-1}$ below 1 K, it is clear that the decrease of linewidth is less pronounced than in the samples of Refs. 7 and 8.

After purification the sample contained ~ 10 ppm substitutional impurities (1 ppm Fe). The linewidth below 1 K had now dropped to

$\sim 0.16 \mu\text{s}^{-1}$, and the results clearly resemble those of the Vitry polycrystal sample [8]. These measurements are compared in Fig. 1, where the Vitry copper linewidth is indicated by the broken line (fitted curve of Ref. [8]). Already from these results it is clear that chemical impurity effects are very important at low temperatures in Cu, a conclusion which is also supported by the result at low temperatures on a Ni-doped Cu sample in Ref. 8. Therefore, the search for effects of isotopic composition should be done in chemically well-defined samples only.

The main experiment aiming at the isotope effect was performed on three samples having undergone the same processes of chemical refinement (see Samples section for details), and therefore containing approximately the same amounts of impurities. The three samples were purified ^{63}Cu , ^{65}Cu and the natural Cu sample. The residual impurity contents of the samples can be found in Table 1. The samples were all of very similar shapes, keeping systematic errors at a minimum, and the measurements restricted to the low-temperature region only (dilution cryostat). The results from the linewidth measurements are given in Fig. 2, where it can be seen that the data on ^{63}Cu can hardly be distinguished from those on the natural Cu sample ($\sigma \approx 0.16 \mu\text{s}^{-1}$ below 0.5 K). It should be pointed out that the two copper isotopes have very similar magnetic moments, and the change of dipolar linewidth from this source alone would not be detectable within the accuracy of the experiment.

The ^{65}Cu measurement gives on the other hand a larger σ ($\approx 0.21 \mu\text{s}^{-1}$). We can however not directly ascribe the higher linewidth in the ^{65}Cu to a pure isotope effect, since we must remember the high sensitivity of the measurements to chemical impurities.

In order to study the chemical impurity effects on the low-temperature region in Cu, the two pure Cu samples were doped with Fe (95 at. ppm) and Si (109 ppm) respectively. These samples were measured in the whole temperature range from 0.1 to 200 K, and the linewidths are presented in Fig. 3. Unfortunately the beam conditions were very unfavourable during these measurements, and the quality of the data is not very good. The effect of the Fe below 2 K is clearly seen, while the effect of

Si-doping appears to be smaller. These two impurities are expected to produce similar lattice distortions in Cu [20]. This indicates therefore that not only the strain field, but also the specific nature of the impurity is important for the results.

The measurements on the two large single crystals were concentrated to 80 mK (at several different magnetic fields), but a few points at higher temperatures were also obtained. The field dependence measurements aimed firstly at a check of the results of Ref. 8, which were obtained with a much smaller sample and might contain systematic errors, and secondly to have a measurement with so small a background that a meaningful evaluation of the lineshape should be possible (even fairly moderate contributions from muons precessing in the cryostat or elsewhere outside the sample could be dangerous to conclusions from lineshape studies).

The results of the field dependence measurement are presented in Fig. 4. The results are similar to those of Ref. 8, except for a generally slightly higher linewidth ($\sigma \approx 0.16$ compared to 0.15 in ref. [8]).

Until now there does not exist any commonly used practical measure of the lineshapes in transverse field μ SR. Normally, the data allow only a one-parameter characterization of the depolarization, i.e. the linewidth parameter is fitted while a certain shape is assumed. In the present study two different modes were employed; In the first method the depolarization function was fitted to $P(t) = P(0)\exp(-(\Lambda t)^x)$, where the exponent x should approach 2 for a pure Gaussian lineshape, and 1 for a Lorentzian (in the limit of fast motional narrowing). In the present study all the 80 mK lineshape parameters x lie between 1.3 and 1.6, which is fully consistent with muons slowly diffusing out of traps (muons diffusing towards traps would have x around 2 or even slightly above 2). However the x parameter is not quite sensitive enough for the present case and another method was adopted here.

The normal analysis interval for the linewidths in μ SR is around 7-8 μ secs. When the analysis is made over a shorter interval (3-4 μ secs) one should in principle obtain the same results, but with larger errors, if the assumed lineshape were correct. In the present study the lineshape

expected for immobile muons is Gaussian, (as verified at 80 K [5]). In our second method a lineshape analysis was made by fitting the spectra with a Gaussian decay on the time intervals from $t = 0$ to $t = 2, 4, 6$ and $8 \mu\text{secs}$. Then a series of μSR spectra were computer simulated for various possible situations. These simulated spectra were of comparable statistics and background level as in the real experiments, and represented the situations of

- a) static but extended muons, (Gaussian lineshape)
- b) slowly diffusing muons (Eqn [1])
- c) muons getting trapped (as proposed in ref. [8]).
- d) static muons distributed on tetrahedral and octahedral sites (as proposed in ref. [11]).

For situations c) and d) the two-state model described by differential equations was used [13]. The simulated spectra were analyzed in exactly the same way as the real data, and they were used as an aid to interpret the results of the lineshape studies.

Fig. 5 shows some results from this interval fitting of the linewidth of the experimental data. From Fig. 5 we can make the following observations:

- a) A common feature is that all the spectra start with a stronger initial depolarization (evaluated for Gaussian lineshape) than what is eventually reached as the average over $6-8 \mu\text{secs}$. This shows that the lineshape is intermediate between Gaussian and Lorentzian, and furthermore that it is in good agreement with an assumption of diffusing muons (as borne out by the simulations). Extended static muons should have given σ 's essentially constant for the different time intervals. On the other hand a distribution on T and O-sites as proposed in [11] also gives a non-Gaussian shape, which could be compatible with the observed lineshape.
- b) In the (100)-direction at 80 mK there is no observable field dependence of the lineshape. This directly rules out any strong contributions from tetrahedral sites, since at 1450 Gauss the depolarization rates would be very much lower for T-sites, whereas at 160 G they are practically identical. A similar independence of field can be inferred from the data in the (111)-direction, but here the overall damping is field-dependent, making the comparison slightly more difficult.

c) Raising the temperature to 2 K increases as expected the total damping after 6-8 μ secs, but we find that the main increase of the linewidth is created already before 2 μ secs. This speaks against the model of diffusion followed by trapping as proposed in ref. 8, but also against the tetra-octa transitions proposed in [11], which in this temperature range resembles the trapping situation.

Thus, within the limits of this lineshape analysis, we find no evidence whatsoever supporting models involving initial tetrahedral sites, or of trapping above 1 K. The time evaluation of the depolarization is however fully compatible with slowly diffusing muons, both at 80 mK and 2 K. Therefore it is justified to derive a correlation time τ_c for the muon jumps from the standard motional narrowing formula

$$P(t) = P(0)\exp \{-2\sigma_o^2 \tau_c^2 (\exp(-t/\tau_c)-1 + t/\tau_c)\} \quad (1)$$

where σ_o , the linewidth in absence of diffusion, was set to $0.25 \mu s^{-1}$. The jump times obtained in this way are $3.5 \times 10^{-6} s$ at 2 K and $1.4 \times 10^{-6} s$ for the plateau between 80 mK and 0.5 K. These numbers are in good agreement with the zero-field data of Ref. [9].

DISCUSSION

Criticism of existing models.

The striking features of the low temperature muon behaviour in Cu are (i) the decrease of linewidth below 5K and (ii) the existence of a temperature independent plateau in the linewidth below 0.5 K. These results have given rise to several partly contradictory explanations. As mentioned above, Stoneham, and later more explicitly Seeger, proposed the involvement of meta-stable tetrahedral sites [10, 11]. Our results contradict this picture, mainly in the 2K region where the lineshape is clearly in disagreement with the proposed model. We also do not find any indications at all of involvement of tetrahedral sites.

In the earlier model proposed by some of the present authors [8], it was assumed that the muon diffuses through a one-phonon process, which does

not depend on temperature for motion in the direction of energetically lower sites at very low T. In this approach the increase of the damping above 0.5 K was thought to be a result of impurity trapping due to enhanced muon diffusion at higher temperatures; however, the data of Ref. [8] did not allow a detailed lineshape analysis.

Our present results at 80 mK which essentially reveal a diffusing muon, are in agreement with Ref. [8] as far as the mobility of the muon is concerned, but the new lineshape results at 2 K are in disagreement with a trapping process. Since low damping should be observed during the initial stage of the muon history, as it diffuses towards the traps, while in a later stage, where the muons are mainly sitting in the traps, a higher damping should be found. Thus, we have to reject also the trapping model [8]. This argument is valid also against the Stoneham-Seeger model, if the meta-stable state is sufficiently extended to give a negligible width.

The zero field measurements reported by Clawson et al. [9] were analyzed in terms of the Kubo-Toyabe depolarization function. Such an analysis allows a distinction between static (but extended) and dynamic muon states. At all temperatures investigated (down to 0.5 K) Clawson's results are in agreement with a slowly diffusing muon, the jump rate of which increases with decreasing temperature. These results are in agreement with our analysis.

Aspects of quantum diffusion in Cu.

From the previous section we conclude that in our purest Cu-samples all muons thermalize at octahedral sites and start out from there to diffuse slowly over the time range covered in our experiments ($\approx 10 \mu\text{s}$).

Fig. 6 shows the trend of the jump rates for Cu as estimated in the present experiment and from Clawson et al. It is compared with the jump rates for muons in Al derived from previous work [12, 21]. Apparently the muon jump rate in Cu passes through a minimum somewhere between 10 and 80 K. The slow increase towards lower T extends down to about 0.5 K, below which the jump rate seems to be temperature independent. With the exception of the low T plateau muon diffusion in Cu and Al shows qualitatively the same features - only the time and temperature scales are shifted with respect to each other.

The only jump process which can give rise to an inverse temperature dependence is the coherent transition (which is suppressed by scattering at higher temperatures) . There is however no quantitative agreement with the existing phonon-scattering theories [22], which predict a T^{-9} dependence for $T \ll T_D$. This discrepancy has already been noticed in low-temperature experiments in impurity-doped Al, where an exponent of $T^{-0.6}$ was obtained empirically [12]. The negative slope in Cu is about the same as in Al in the T-dependent region, but the jump rate is 10^3 - 10^4 times higher in Al. The ratio between the rates in Cu and Al should reflect the ratio of the effective tunnelling matrix elements $[J_{\text{eff}}(\text{Cu})/J_{\text{eff}}(\text{Al})]^2$ multiplied by factors describing the scattering reduction in the jump rates which may differ for the two metals. The jump rate minima (between 10 and 80 K for Cu and ≈ 2 K for Al) occur at temperatures which in this interpretation represent the transition from a coherent to an incoherent regime in the two metals.

From the high T diffusion data where the diffusion is due to incoherent tunneling-hopping, the matrix elements J for Cu and Al have been derived to be $J(\text{Cu}) \approx 18 \mu\text{eV}$ and $J(\text{Al}) \approx 1000 \mu\text{eV}$, respectively [23, 12]. After correction for the effect of the distortion cloud, effective tunneling matrix elements of the order of $J_{\text{eff}}(\text{Cu}) \approx 1 \mu\text{eV}$ and $J_{\text{eff}}(\text{Al}) \approx 100 \mu\text{eV}$ were estimated. Thus the ratio $(J_{\text{eff}}(\text{Cu})/J_{\text{eff}}(\text{Al}))^2 \approx 10^4$ is in rough agreement with the observed ratio of the (low T) jump rates in the negative slope region. We should like to emphasize that this agreement is not trivial since the matrix elements are taken from high T diffusion and applied to a completely different range.

The low-temperature plateau

The temperature independent region below 0.5 K in Cu has been reproduced with several sufficiently pure samples of different origin and $\sigma = 0.15$ - $0.16 \mu\text{s}^{-1}$ appears to be a natural lower limit for the effects of chemical purification. It is surprising, however, that this limit also seems to be independent of isotopic composition since in the framework of conventional strain theory, the isotope effects should be at least as large as the impurity effects at the concentrations considered here.

There are essentially two different possibilities to explain this low T plateau:

(i) Firstly, it could be a result of an intrinsic upper limit of the small polaron transition probability. At very low temperatures where the phonon scattering rate becomes much lower than τ_{μ}^{-1} , the observed coherent transitions are limited only by the polaron transition probability itself, which is of the order of $(\tau_{\text{coh}})^{-1}_{T=0} = J_{\text{eff}}/\hbar$. Thus, as pointed out for instance by Petzinger [24], the jump rate should level off and be T-independent at sufficiently low temperatures. This low T-level of τ_c^{-1} depends strongly on the host material. An order of magnitude estimate gives 10^9 s^{-1} for Cu and 10^{11} s^{-1} for Al. This estimate is still three orders of magnitude higher than observed for Cu - ($\sim 10^6 \text{ s}^{-1}$). However the fact that the jump rates in pure natural Cu and ^{63}Cu are practically identical bears evidence for the existence of an intrinsic limit for μ^+ diffusion in Cu.

(ii) Secondly, the T-independence of the jump rate below 0.5 K could be caused by static disorder, which as well as thermal fluctuation could set an upper limit for muon coherent diffusion. As mentioned earlier the static disorder may arise from the isotope mixture or from chemical impurities. In the following we give some estimates for the disorder due to strains for the cases of

- a) 1200 ppm ^{65}Cu in ^{63}Cu
- b) 100 ppm Fe in Cu
- c) natural isotopic mixture of Cu

We start then from the strain formula for point defects [25]

$$E_{\text{int}} = -\frac{1}{r} \frac{15}{8\pi} \delta \left[\frac{\bar{C}_{11} + \bar{C}_{12}}{3 \bar{C}_{11}} \right] \Delta V^{\mu} \Delta V^d \times \left[\frac{3}{5} - \sum_j \rho_j^4 \right] \quad (2)$$

where ΔV^{μ} and ΔV^d are the volume changes produced by the muon and the defects. Proceeding in the same way as in Ref. [12], and introducing the elastic constants for Cu we find the difference in energy levels of two sites separated by a distance d , at the distance r away from the impurity

$$\langle \Delta E \rangle \approx 1.04 \cdot \Delta V^d \cdot \frac{d}{r^4} \quad (3)$$

in units of eV.

In the case of chemical impurities, ΔV^d can be found from measured lattice dilatations. For isotopic Cu impurities in a ^{63}Cu lattice (or vice versa) we have estimated the volume change from the zero-point vibrational amplitudes ($\approx 0.05\text{\AA}$) and their changes with the mass of the atom.

Evaluating the disorder $\langle \Delta E \rangle$ at a distance r half-way between the impurities we obtain

$$\langle \Delta E \rangle \approx 5 \text{ } \mu\text{eV} \text{ for } 1200 \text{ ppm } ^{65}\text{Cu in } ^{63}\text{Cu}$$

$$\langle \Delta E \rangle \approx 5 \text{ } \mu\text{eV} \text{ for } 100 \text{ ppm Fe in Cu}$$

For the natural isotope mixture this formula does not apply because of the random overlap of strains from nearby isotopes, but an extrapolation leads to ΔE well above $100 \text{ } \mu\text{eV}$ (this value was also given in Ref. 14). Since the effective matrix element J_{eff} for small-polaron transitions can be estimated to be $\approx 1 \text{ } \mu\text{eV}$ for Cu, long range coherent diffusion should be impossible in natural Cu. However, it should be noted that coherent transitions do not necessarily involve an extension of the wave function over a large volume, but can in fact involve only a single jump. The main point is that there is no exchange of phonons with the lattice in the transition. The jump rates in Cu are so slow ($\approx 10^5\text{--}10^6 \text{ s}^{-1}$) in the actual temperature range that on the average only one or a few transitions occur over the time of observation. The limitation of coherent processes (phonons, elastic strains, conduction electron scattering [12]) has in most theories been evaluated for the percolation limit, as for instance concerning the Mott transition for electronic conduction. Single coherent transitions for muons may be less sensitive to local strain inhomogeneities than predicted by the Anderson condition.

As an example we consider the situation in natural Cu where the disorder is caused by the difference in isotope mass. If the two isotopes are considered to be statistically distributed on the Cu-sites and only nearest neighbours are taken into account, we obtain a probability $P \approx 0.3$ that two adjacent O-interstices are surrounded by the same isotope configuration. The probability is $P = 0.1$ for two successive steps and it drops very fast for higher orders. Since the coordination number is as high as 12 a few jumps might thus be probable even for $\langle \Delta E \rangle > J$.

The remaining possibility for a few jumps may explain why σ is insensitive to the isotope concentration over such a large range (1,2 % for the ^{63}Cu -sample, 31% for the natural composition). The difference observed for the ^{65}Cu sample (2.3 %) may very well be due to the different impurity concentration in this sample as discussed later.

The present evidence therefore seems rather to support the view that the isotope composition is unimportant for the observed diffusion process and that the $\sigma = 0.16$ limit (or $\tau_c \approx 10^6$ limit) is not set by the strain effect. However, in order to definitely establish the role of the isotope mixture it would be necessary to decrease the isotopic impurity still looking for a lowering of σ .

Influence of chemical impurities

The effect of chemical impurities on the observed low T linewidth are relatively much stronger. The addition of 100 ppm Fe and 200 ppm Ni [8] raises the σ -value from 0.16 (μs^{-1}) to 0.22 (μs^{-1}) and 100 ppm Si to 0.19 (μs^{-1}). From the application of the strain field formula we find that the disorder created midway between the impurities should be much less important than that present in natural copper. Thus the strong influence of impurities on σ in natural Cu cannot be related to the disorder produced by the impurities, but it can instead be initial [10]. It is more probable that a certain fraction of the muons is localized near the Fe and Ni impurities by a capture controlled trapping process which is independent of T and proportional to the impurity concentration. From the observed change of linewidth at 100 ppm Fe we estimate this fraction to be of the order of 60% while the rest are self-trapped by ordinary thermal processes. The Si impurities on the other hand seem to be less attractive in such a picture of catalyzed localization, which is in agreement with what was suggested by Browne and Stoneham [10].

In this context we note however that the 17 ppm Fe concentration in the ^{65}Cu sample appears too weak to raise the low-temperature level to the observed $0.20 \mu\text{s}^{-1}$, unless the preferred localization is a non-linear function of impurity concentration.

The case of Fe-impurities need some specific considerations since they may show localized electronic magnetism (although we are all the time below the Kondo temperature for Fe in Cu, $T_K \approx 30$ K). We estimate that the Fe moment contributes to the observed linewidth only in the case when the Fe atom is next neighbour to the muon. Such a magnetic contribution should tend to decrease with decreasing magnetic field, while the observed σ at 100 mK increases slightly when the field is lowered from 120 G to 70 G. Although not conclusive, this fact together with previous indirect indications of large trapping radii for muons around impurities leads us to believe that the observed linewidth originates from the copper nuclear dipoles only.

CONCLUSION

In this paper we have discussed the results of several different measurements related to the problem of the decrease of linewidth in Cu at low temperatures. From the detailed lineshape analyses of the spectra from large single crystals we deduce i) the muons are mobile at low temperature ii) previous models involving meta-stable tetrahedral sites are not compatible with the experimental data iii) there is no evidence for trapping in the 2 K-region - the data instead point to a diffusion rate which is simply increasing when going down from 10 K to 0.5 K.

The inverse temperature dependence of the diffusion indicates a coherent tunnelling process. The temperature dependence between 0.5 K and ~ 10 K is slow, with $\tau_c^{-1} \propto T^{-0.7}$, which resembles the situation in Al below 1 K. In addition there is a limitation for the μ^+ diffusion in Cu below 0.5 K.

The experiments on isotope separated Cu do not reveal any strong dependence on isotopic composition. We have discussed two possible explanations for the limitation of the jump rate at lowest temperatures: a) limitation by static disorder and b) limitation by maximum velocity possible for the muon wave-packet in Cu. If the diffusion is limited by the disorder created by isotopic mixture, we should have observed a difference between the various compositions. The ^{65}Cu (2.3 o/oo isotope purity) gives a higher linewidth than the ^{63}Cu (1.2 o/oo) in accordance with this picture, but the agreement between natural Cu and the ^{63}Cu strongly indicates that the limitation is independent of isotope disorder.

At present we cannot therefore decide between these explanations. A decisive experiment would be to carry out new experiments on samples with several intermediate isotopic compositions keeping the amount of chemical impurities as low as possible.

The effect of Fe (and Ni) impurities is very strong for the low-temperature diffusion in Cu, while Si impurities give a lower effect. We interpret the strong influence of Fe and Ni as being due to the effect of preferred initial localization close to these impurities, while the effect of the strain disorder created by these impurities appear to be only of secondary importance.

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FIGURE CAPTIONS

- Fig. 1 Gaussian damping rate σ in the ^{63}Cu sample before and after purification. The broken line indicates the Vitry sample linewidth of Refs. [7-8] (result of the model fit in Ref. [8]).
- Fig. 2 Gaussian damping rates σ in the ASARCO natural Cu sample, and the purified ^{63}Cu and ^{65}Cu samples.
- Fig. 3 Comparison of linewidths in natural Cu doped with Fe or Si impurities.
- Fig. 4 Gaussian damping rates σ as function of magnetic field in single crystal Cu at 80 mK.
- Fig. 5 Interval analysis of the damping in single crystal Cu. The fits are made with Gaussian lineshape on different analysis intervals t_A , and shows the strong deviations from the pure immobile muon lineshape.
- Fig. 6 Comparison of muon jump times in Cu and Al, assuming coherent diffusion below ~ 30 K and ~ 2 K respectively. The Al data are derived from Refs. [12] and [21].

^{63}Cu		^{65}Cu		Cu A-58	
starting 1) purified3) material		starting 1) material	purified3) material	starting2) material	remelted3) Cu Kabel-und metallwerke
^{63}Cu	99.6	99.88	.8		3)
^{65}Cu	.4	.12	99.2	.23 99.77	
C				40	
N		3.0	1.3	3.1	1.3
O		2.0	2.3	1.0	4.5
Na		1.0	.7		1.7
Mg				< 0.5	
Al		3.7	8.7	2.2	
S	98	13.2	2.0	1.8	
Cl				.3	
K		1.5		1.8	
Ca			.2	.2	
Ti			.1		
V		.5			
Cr		.6			
Fe	147	1.0	151	< 1 .7	1.6 0.95
Co		.1			
Ni	54	.7	111		
Zn	<40		<40		
As	< 4		< 4		
Ag		.6			
Sn	16		16	.3	0.55
Sb	<32		<32		
Pt		5.4			
Pb	< 3				
Bi	< 3			.1	

analysis 1) Technabexport 2) Asarco 3) ZCH, KFA Jülich

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6