Muon diffusion in ultrapure copper and bismuth

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The rate of spin relaxation has been measured as a function of temperature for a positive muon in ultrapure specimens of copper and bismuth. The measured dependence for bismuth is compared with the theoretical result for coherent muon diffusion in a crystal lattice with shifted levels.

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§1. INTRODUCTION

The diffusion of positive muons (μ^+ mesons) in metals has attracted attention because there are a number of features that distinguish this process from the diffusion of the heavier, singly-charged particle—the proton. Even early work in this field showed that muon diffusion was a sub-barrier process involving transitions between neighboring intersitial voids in the crystla lattice of the metal. Moreover, it is well known that proton diffusion is an over-barrier Boltzman transition between two positions with minimum potential energy (two voids). It was eventually found that muon diffusion depended on the purity of the metal. Extraneous impurities distort the crystal lattice of the metal, forming traps for the diffusing muon. For most metals, even a small amount of impurity (10^{-4}–10^{-5}) leads to a change in the diffusion mobility of muons. This effect may also be due to small deformations of the crystal lattice at large distances from the impurity.

Experimental studies of sub-barrier muon diffusion have opened up new possibilities for measurements of fundamental parameters characterizing the tunneling process, e.g., the transition matrix element and magnitude of the polaron effect. Experiments with metals containing known amounts of impurity are imortant sources of information that contribute to our understanding of the process of localization of the diffusing muon. However, the most important experiments at present are those in the diffusion of muons in ultrapure metals in which the uncontrollable effect of impurities and other lattice defects is reduced to a minimum.

We have carried out an experimental investigation of the diffusion of positive muons in ultrapure specimens of copper and bismuth. Muon diffusion was investigated by measuring the variation in the rate of relaxation Λ of the muon spin. As the muon diffuses through the crystal lattice of the metal, the local magnetic fields acting upon it become functions of time, and this leads to a reduction in Λ. The maximum rate of relaxation should be observed for a nondiffusing muon. It is natural to expect a reduction in Λ at high temperatures at which there is an increase in the rate of diffusion. However, a substantial reduction in Λ is observed in copper,[1] even at low temperatures $T < 2$K. A still more complicated temperature dependence $\Lambda(T)$ is observed for bismuth.[2] These results were obtained for very pure single-crystal specimens of these metals. The impurity density in the copper and bismuth specimens was $\sim 10^{-3}\%$ and $\sim 10^{-2}\%$, respectively. The copper and bismuth specimens used in our measurements had still lower impurity densities. The experimental temperature dependence $\Lambda(T)$ for bismuth was compared with the theoretical function $\Lambda_{\text{theor}}(T)$ that describes the coherent diffusion of a muon in a crystal lattice with shifted levels.

The experiments were performed on the synchrocyclotron of the Leningrad Institute of Nuclear Physics of the Academy of Sciences of the USSR at Gatchina.

§2. EXPERIMENT

The copper specimen consisted of seven individual single-crystal cylinders 10 mm in diameter and 30 mm long. The bismuth specimen was an annealed polycrystal with grain dimensions 10–15 mm. The residual resistance $\gamma = R(T = 300\ \text{K}/R(T = 4\ \text{K})$ of these copper and bismuth specimens were $\gamma_{\text{Cu}} = 52\,000$ and $\gamma_{\beta i} = 900$. The dislocation densities were: $n_{\text{Cu}} = 10^6\ \text{cm}^{-2}$, $n_{Bi} = 10^3 - 10^4\ \text{cm}^{-2}$. The table lists the impurity densities measured by a mass-spectrometric method.

Figure 1 and 2 show the measured temperature dependence $\Lambda(T)$ for ultrapure copper and bismuth specimens. For comparison, they also show the earlier measurements of $\Lambda(T)$ for less pure bismuth[2] and copper[3] specimens containing $\sim 10^{-2}\%$ and $10^{-3}\%$ of impurities. The values of Λ shown in Figs. 1 and 2 were determined from the damping of the muon spin precession amplitude in a transverse magnetic

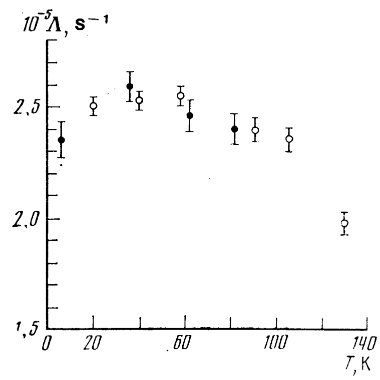

FIG. 1. Rate of relaxation $\Lambda(T)$ of muon spin in copper: ●—ultrapure specimen; ○—polycrystalline specimen with $\sim 10^{-3}\%$ impurity.

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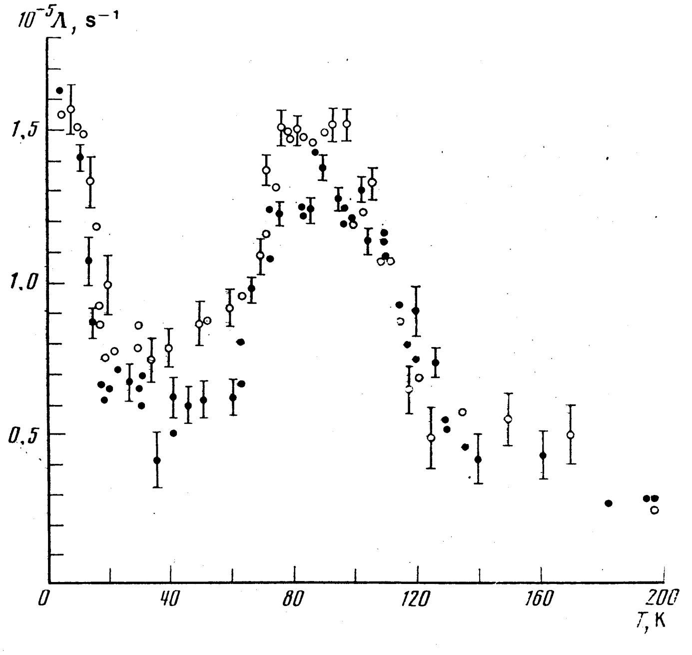

FIG. 2. Rate of relaxation $\Lambda(T)$ of muon spin in bismuth: ●—ultrapure specimen; ○—specimen with $\sim 10^{-2}\%$ impurity.

field $H = 70$ Oe by using the method of maximum likelihood to fit the experimental precession data to the theoretical expression

$$N(t) = N_0 e^{-t/\tau_0}(1 + a e^{-\Lambda^2 t^2} \cos \omega t), \qquad (1)$$

where $N(t)$ is the number of decay positrons $u^+ \to e^+$ emitted in the direction of the initial polarization of the muon, $\tau_0 = 2.2\ \mu$s is the muon lifetime, a is the experimental asymmetry coefficient of the angular distribution of positrons from $u^+ \to e^+$ decays, and $\omega = eH/m_u c$ is the Larmor precession frequency of the muon spin in the field $H = 70$ Oe. It follows from (1) that the muon spin relaxation rate Λ was determined from the Gaussian time dependence $P(t) = e^{-\Lambda^2 t^2}$ of the muon polarization. The Gaussian shape of $P(t)$ should be observed in the absence of muon diffusion. For a diffusing muon, the function $P(t)$ has a complicate shape[4] but tends asymptotically to an exponential function of time as the rate of diffusion increases. For the sake of uniformity, Figs. 1–4 show the $\Lambda(T)$ dependence under the assumption that $P(t) = e^{-\Lambda^2 t^2}$, i.e., in accordance with (1) throughout the temperature range under investigation.

The function $\Lambda(T)$ shown in Fig. 1 for ultrapure copper was determined experimentally only at low temperature $T < 80$ K, where one would expect to see evidence for the coherent mechanism of muon diffusion. It is clear from Fig. 1 that the $\Lambda(T)$ dependence for copper with $\sim 10^{-3}\%$ of impurity is the same as for ultrapure copper with $\lesssim 10^{-4}\%$ of impurity. Hence, it may be concluded that the muon spin relaxation in copper at temperatures in the range $T = 6$–80 K is unrelated to the presence of impurities with densities in the range $10^{-3} - 10^{-4}\%$. This conclusion is in agreement with the fact that the calculated and experimental values of Λ for copper are equal if it is assumed that, at temperatures $T = 6$–80 K, the muon does not diffuse but is localized in an octavoid of the crystal lattice of the metal.[5]

It is clear from Fig. 2 that the temperature dependence $\Lambda(T)$ obtained for the ultrapure bismuth specimen is somewhat different from the corresponding result for bismuth containing $10^{-2}\%$ of impurities. Moreover, it is also clear from Fig. 2 that this difference is small and that the shapes of Λ (T) are similar for both bismuth specimens. The temperature dependence $\Lambda(T)$ for ultrapure bismuth emphasizes still further the basic features established for the less pure specimen: there are two plateaus, one at $T = 20$–65 K and the other at $T = 75$–100 K, and Λ undergoes a rapid variation at $T = 10$–20 K and $T = 65$–75 K. The differences between the $\Lambda(T)$ obtained for the two specimens indicate that the non-

Table I. Impurity concentrations in the ultrapure copper and bismuth specimens

Impurity	10^{-5} at %	Impurity	10^{-5} at %	Impurity	10^{-5} at %	Impurity	10^{-5} at %
	Copper				Bismuth		
Na	<2	Co	<0.2	Si	<3	Sn	<0.6
Mg	<3	Zn	<0.7	Mg	<9	V	<1
Al	<3	As	<0.3	Cu	<4	B	<0.6
Si	<3	Nb	<0.1	Cd	<0.6	P	<20
P	<0.2	Mo	<0.6	As	9	Mn	<1
S	<3	Ba	<0.8	Ba	<0.5	Fe	<1
Cl	<0.4	W	<1	Be	<0.7	Pb	<0.3
Cr	<0.2	K	<1	Co	<1	W	<4
Mn	<0.2	Ag	<1	Cr	<1	Mo	<0.7
Fe	<3			Ni	<1	Ca	<2

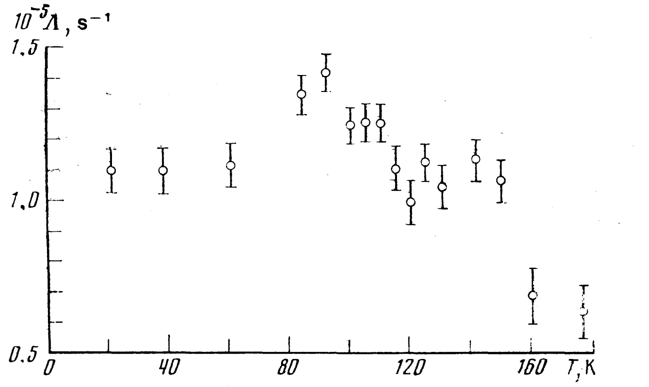

FIG. 3. Rate of relaxation $\Lambda(T)$ of muon spin in the alloy Bi + 1% Sb.

monotonic shape of $\Lambda(T)$ obtained for bismuth is connected with the presence of the impurities, but even the maximum possible degree of purificationof the metal (see the table) produces practically no reduction in this nonmonotonic behavior. Figure 3 shows $\Lambda(T)$ for the alloy Bi + 1% Sb. Comparison of Figs. 2 and 3 shows that the addition of 1% antimony has a considerable effect on muon diffusion in bismuth. This can be seen, in particular, in the disappearance of the characteristic valley on the $\Lambda(T)$ curve at $T = 10$–70 K.

§3. THEORETICAL DESCRIPTION OF MUON DIFFUSION IN BISMUTH

The experimental functions $\Lambda(T)$ shown in Fig. 2 for bismuth can be described qualitatively within the framework of the theory of diffusion of particles in nonideal crystals that was developed in the last few years.[6–8] According to this theory, in a strictly regular crystal at $T = 0$, sub-barrier tunneling of particles between neighboring equivalent interstices leads to motion within band width $z\Delta$, where Δ is the transition amplitude and z is the number of equivalent interstices in the nearest coordination sphere. The band width for muons turns out to be very small: $z\Delta \ll \Theta$ in all cases Θ is the Debye temperature) and, as a rule, $z\Delta < T$. For finite T, the interaction with phonons is found to slow down the diffusion process. However, even for small $T \ll \Theta$, relative fluctuations in the energy levels in neighboring interstices begin to exceed the bandwidth. This leads to the dynamic disturbance of the band motion. A coherent transition (in which tunneling occurs without the excitation of phonons) will then effectively occur only at a time of random coincidence of the levels. As the temperature increases, the probability of such a coincidence decreases, and this leads to a sharp reduction in the diffusion coefficient with temperature T. At low temperatures, noncoherent diffusion (in which tunneling is accompanied by the excitation of phonons) turns out to be negligible in comparison with coherent diffusion.

In a nonideal crystal, the situation is essentially different.[8] The small width of the coherent band ensures that, in a relatively large region around an individual defect, the energy levels in neighboring interstices are shifted by an amount exceeding $z\Delta$. Evan a tlow densities of defects, the regions of this statistical level shift are found to overlap, which leads to the localization of the majority of the muons at $T \to 0$, and this occurs mainly in regions well away from the defects. It is precisely in this wasy that one can explain the observed localization in bismuth for $T < 10$ K.

As the temperature increases, dynamic level fluctuations can effectively compensate for the statistical shifts, and this opens up the possibility of a coherent transition, and thus eliminates the localization. In contrast to the ideal situation, diffusion will now increase with increasing T, and this will occur at a very high rate. It is precisely this picture that is observed in bismuth at temperatures in the range 10–20 K, and this is reflected in the very rapid reduction in the rate of relaxation Λ (see Fig. 2).

When the dynamic level shift begins to exceed the static shift, the increase in temperature should lead to a slowing down of coherent diffusion, just as in the ideal crystal. This, in turn, should result inan increase in depolarization, i.e., an increase in Λ, which is, in fact, observed for $T > 65$ K. Parallel channels of diffusion and classical over-barrier diffusion, should become important as the temperature increases further. Both these channels lead to an activated increase of the diffusion coefficient. For this reason, the localization of particles due to the dynamic level shift at $T \approx 75 - 100$ K is replaced by activated delocalization, and this is observed for $T > 100$ K.

In the genral case, the reciprocal of the lifetime of a muon in an individual elementary cell can be written in the form

$$1/\tau = 1/\tau_{\text{coh}} + 1/\tau_{\text{noncoh}}, \tag{2}$$

where the first term represents the departure of the muon from the cell as a result of coherent diffusion, and the second represents a noncoherent and classical jump. When the static (ε) or the dynamic ($\Omega(T)$) level shifts exceed the band width, the temperature dependence of $1/\tau_{\text{coh}}$ is given by

$$\frac{1}{\tau_{\text{coh}}} \approx \frac{z\Delta^2}{\hbar} \sum_g \frac{\Omega(T)}{\varepsilon_g^2 + \Omega^2(T)} \approx \frac{z\Delta^2}{\hbar} \frac{\Omega(T)}{\varepsilon^2 + \Omega^2(T)}, \tag{3}$$

where

$$\Omega(T) = \xi k \Theta \left(\frac{T}{\Theta}\right)^9 \int_0^{\Theta/T} \frac{x^8 e^x\, dx}{(e^x - 1)^2}. \tag{4}$$

In this expression, k is the Boltzmann constant and ξ is a numerical parameter of the order of unity. Expression (4) is determined by the mean square relative level fluctuations, which are dominated in this particular temperature range by two-phonon processes (the above expression was obtained in the Debye approximation). The sum in (3) is evaluated over the nearest equivalent (in the ideal lattice) interstices. The quantity ε in (3) is a certain average level shift, evaluated over the nearest coordination sphere. In principle, ε will vary from point to point in a nonideal crystal.

At sufficiently low temperatures at which $\Omega(T) \ll \varepsilon$, we have

$$\frac{1}{\tau_{\text{coh}}} \approx \frac{z\Delta^2}{\hbar} \frac{1}{\varepsilon^2} \Omega(T). \tag{5}$$

It follows from this expression that the temperature dependence $\tau_{coh}(t)$ is a universal function at low T. The nature of the distribution of defects (level shifts) is eventually represented by a certain ε_{eff} averaged over space. When $T \ll \Theta$, we have $1/\tau_{coh} \propto T^9$. Conversely, for $\Omega(T) \gg \varepsilon$,

$$\frac{1}{\tau_{coh}} \approx \frac{z\Delta^2}{\hbar\Omega(T)}. \tag{6}$$

This expression is independent of whether the crystal is nonideal or not.

In the intermediate region, for which $\Omega(T) \sim \varepsilon$, the effective dependence of $1/\tau_{coh}$ on T is not universal and is very sensitive to the procedure used to average over the distribution of the level shifts. With increasing T and, hence, increasing $\Lambda(T)$, transitions with larger ε come into play, so that averaging should lead to an effective flattening of the dependence of $1/\tau_{coh}$ on T in this intermediate region. This may be the cause of the flat region on $\Lambda(T)$ in the temperature range 20–65 K in Fig. 2.

In the quantitative comparison between theoretical and experimental results, we have ignored the precise averaging procedure and have simply adopted a fixed value $\varepsilon = \varepsilon_{eff}$ in (3). We assume, for the sake of simplicity, that $1/\tau_{noncoh}$ was determined by a single channel of activated motion, so that

$$1/\tau_{noncoh} = \nu e^{-U/T}. \tag{7}$$

The theoretical function $\Lambda_{theor}(T)$ shown in Fig. 4, together with the experimental data, was obtained by taking $\tau(T)$ in accordance with (2) after extrapolation of the time dependence of the polarization of the diffusing muons

$$P_{diff}(t) = \exp[-2\sigma^2\tau^2(e^{-t/\tau} - 1 + t/\tau)] \tag{8}$$

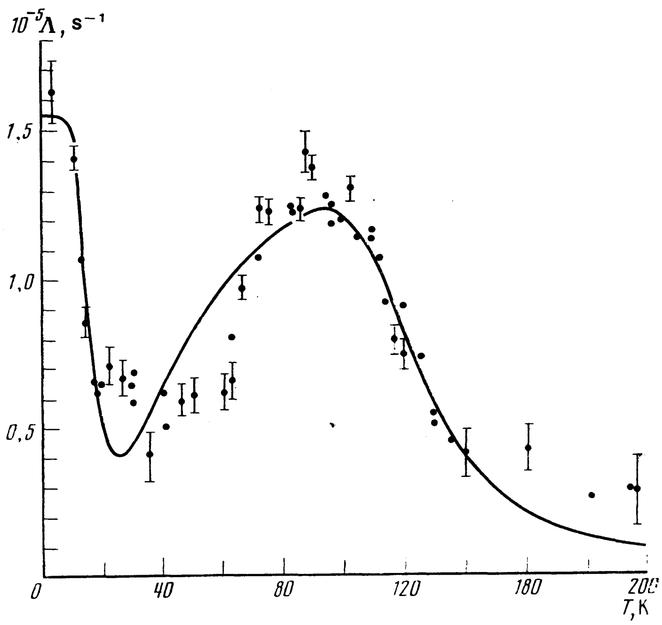

FIG. 4. Comparison of experimental and theoretical functions $\Lambda(T)$ for the ultrapure bismuth specimen. The solid curve represents the theoretical function $\Lambda_{theor}(T)$ with parameters given by (9) and (10).

to the Gaussian function

$$G(t) = \exp[-\Lambda_{theor}^2 t^2].$$

The value $\sigma = \Lambda(T \to 0) = 0.155\ \mu s^{-1}$ was adopted in accordance with the experimental value of Λ for $T < 10$ K. The parameters ε/ξ, $z\Delta^2/\xi$ and U, ν were found by comparison with experimental data. Each pair of parameters was determined practically independently of the temperature dependence $\Lambda(T)$ in different temperature intervals. Thus, comparison with the high-temperature reduction in $\Lambda(T)$ gave:

$$U = (1470 \pm 70)\ \text{K}, \quad \nu = 10^{11.3 \pm 0.1}\ \text{s}^{-1}. \tag{9}$$

The corresponding comparison in the temperature range $0 < T < 100$ K gave

$$\varepsilon_{eff}/\xi = (0.34 \pm 0.04)\ \text{K}, \quad z\Delta^2/\xi = (1.9 \pm 0.2)\,10^{-5}\ \text{K}^2. \tag{10}$$

It is important to note that these parameter values are self-consistent. In fact, if we suppose that $\xi \simeq 1$, we find from (10) that $\Delta \sim 10^{-3}$ K, so that $T > \varepsilon_{eff} \gg z\Delta$, as assumed in the derivation of the theoretical relationships. The numerical value of ε_{eff} is in qualitative agreement with the high purity of our bismuth specimens. If we suppose that the relative level shift at the average distance between point defects can be approximately described by[9]

$$\varepsilon \sim \varepsilon_0 C^{4/3},$$

where ε_0 is of the order of 1 eV and C is the defect density, we obtain

$$C < 10^{-3}.$$

This estimate is in agreement with the experimentally established disappearance of the valley on the function $\Lambda(T)$ when 1 at.% of antimony was introduced into bismuth (see Fig. 3).

The high value of U in (9) indicates that the high-temperature muon diffusion is bismuth for $T > 100$ K is predominantly of the classical over-barrier type. The assumption of sub-barrier noncoherent diffusion for $T > 100$ K would result in a very large polaron effect. It is well known that polaron narrowing of the band width is described by

$$\Delta = \Delta_0 e^{-\Phi(T)}.$$

The factor $\Phi(T = 0)$ can be estimated[8] from the activation energy for sub-barrier noncoherent diffusion ($\Phi = 120$ K)

$$\Phi(T=0) \approx 2U/\Theta = 25.$$

This value of $\Phi(T = 0)$ cannot be reconciled with a reasonable value of Δ_0 if we recall that $\Delta \sim 10^{-3}$ K.

It is important to note that attempts to take into account the polaron band narrowing have not led to reasonable improvement in the agreement between experimental and theoretical values but, on the contrary, have led to $\Phi(T = 0) < 1$, within the framework of the converse problem. It is also noteworthy that ν is less than the standard value. It is possible that this is connected with the complex potential relief typical of a muon in the elementary cell of bismuth.

Thus, the experimental and theoretical pictures are, to a considerable extent, consistent with one another. On the other hand, the above simple variant of the theory with a fixed value of ε_{eff} does not provide a quantitative description of the observed flattening of the function $\Lambda(T)$ in the temperature range 20–65 K (see Fig. 4). A more rigorous analysis will be necessary before we can verify that explicit allowance for the spatial distribution of the level shifts, which is responsible for the flattening of the function $\Lambda(T)$ (see above), will provide a quantitative description of $\Lambda(T)$ in the intermediate region.

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