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Muonium states in germanium

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An anomalous muonium state similar to that in silicon has been found in germanium. This state can be described by an anisotropic hyperfine interaction with the parameters $A_\perp/h = 130.7 \pm 1$ MHz and $A_\parallel/h = 26.8 \pm 1$ MHz. In contrast to Si this anomalous muonium state in Ge was not observed at low external fields. In addition, a detailed investigation of normal muonium in Ge was carried out. For undoped Ge the hyperfine constant is found to be temperature independent in the range between 6 and 81 K with an average value of $A(\mathrm{Ge})/h = 2361 \pm 3$ MHz or $A(\mathrm{Ge})/A(\mathrm{vac}) = 0.5290 \pm 0.0007$. The present value is considerably lower than that published by Gurevich *et al.* The relaxation rate of normal muonium in the Ge sample investigated increases sharply above about 50 K with an activation energy of 14 meV. A correlation with the thermal activation of impurity charge carriers is suggested.

I. INTRODUCTION

If a positive muon is stopped in a target it may capture an electron and form muonium, a hydrogenlike atom. Since the reduced mass of muonium is about the same as that of hydrogen, many properties of muonium and hydrogen, e.g., size and ionization energy, are similar. Therefore in many respects muonium can be considered as a light isotope of hydrogen and the muonium results presented in this paper are expected to hold also for hydrogen under the same conditions.

The formation of muonium is observed by the precession pattern of the muon spin under the influence of the bound electron. In a muon-spin-rotation (μSR) experiment[1,2] the positrons from the anisotropic muon decay ($\tau = 2.2\ \mu$s) are recorded and the precession frequencies of the muon spin can be derived from the time-dependent count rate.

In silicon, two different muonium states, normal and anomalous muonium,[3,4] were observed, whereas in Ge only the normal muonium had been found.[5] From the similarity of the two elements such a difference is not expected and prompted the present investigation. In experiments with high statistics, we succeeded in detecting weak signals which could be assigned to the anomalous muonium in Ge. A description of the properties of this state in Ge and a comparison with the equivalent state in Si is presented in the first part of this paper.

In the second part, a detailed investigation of the normal muonium in Ge, in particular the measurement of the hyperfine constant and the relaxation rate as a function of temperature is reported. These results provide a quantitative basis for the known phenomenon, that the muonium signals disappear at higher temperatures.

First studies on muonium formation in Si and Ge were reported by Feher *et al.*[6] and subsequently by Eisenstein *et al.*[7] These authors measured the residual muon polarization as a function of a longitudinal magnetic field. For highly doped samples or high temperatures little depolarization was observed. However, for low doping and low temperatures an almost complete depolarization was reported, indicating the formation of muonium.

A direct proof of the formation of long-lived muonium states by observing the characteristic muonium precession pattern in transverse fields was reported by Gurevich *et al.*[5] for Ge and by Brewer *et al.*[3] for Si. Both experiments were performed at 77 K. The measured precession frequencies as a function of the external field B could be described by a spin Hamiltonian with an isotropic hyperfine interaction.

$$H_{\mu^+e^-} = A\,\vec{S}\cdot\vec{I} - g_\mu\mu_\mu\vec{I}\cdot\vec{B} - g_e\mu_B\vec{S}\cdot\vec{B}\ . \qquad (1)$$

$\vec{I}$ and $\vec{S}$ are spin operators of the muon and the electron, respectively, and the last two terms describe Zeeman energies. The hyperfine constant A is proportional to the electron density $|\psi(0)|^2$ at the muon site. The values reported for Ge and Si are $A(\mathrm{Ge}) = (0.58 \pm 0.02)A(\mathrm{vac})$ and $A(\mathrm{Si}) = (0.45 \pm 0.02)$

$\times A$(vac). The reduction of A with respect to the vacuum value A(vac) may be understood from a cavity model, proposed by Wang and Kittel.[8] In this model, the muonium is assumed to occupy an interstitial site. The vicinity of the muon within a radius R is treated as vacuumlike. Outside R the electron is assumed to move in a dielectric environment with a macroscopic dielectric constant ϵ. The results are in reasonable agreement with experiment and indicate, that muonium forms a deep level.

Besides the normal muonium state described above additional frequencies were observed in Si and were attributed to an anomalous muonium state, $(\mu^+e^-)^*$.[3,4] The field dependence of these frequencies could be well described by a spin Hamiltonian with a strongly anisotropic hyperfine interaction

$$H_{(\mu^+e^-)^*} = A_\perp (I_x S_x + I_y S_y) + A_\parallel I_z S_z - g_\mu \mu_\mu \vec{I}\cdot\vec{B} - g_e \mu_B \vec{S}\cdot\vec{B} \ . \quad (2)$$

The symmetry axis z is parallel to one of the four equivalent [111] directions in the diamond-type lattice. At present, no physical explanation has been given for the hyperfine constants $A_\perp$, $A_\parallel$. Their values were found to be $A_\perp/h = 92.1 \pm 0.3$ MHz and $A_\parallel/h = 17.1 \pm 0.3$ MHz.

Although the spin Hamiltonians (1) and (2) for the normal and anomalous muonium state, respectively, look quite similar, it should be stressed that the observed μSR signals correspond to quite different transitions among the possible states. In the case of the normal muonium state, the hyperfine constant A is of the order of 2000 MHz and the μSR experiments are performed in the low-field region (up to 0.02 T). In this Zeeman region, all of the four states are coupled, and in a transverse field experiment all four frequencies with $|\Delta M| = 1$ can in principle be observed. The amplitudes for these four transitions are about the same, but the two frequencies corresponding to singlet-triplet transitions are too high to be resolved in the experiments. For increasing field strength, also the other two frequencies exceed the highest resolvable frequency of about 550 MHz.

The hyperfine constants $A_\perp$ and $A_\parallel$ for $H_{(\mu^+e^-)^*}$, on the other hand, are two orders of magnitude smaller than A. This implies, that for a field strength above about 0.02 T, among the four states, those with different electron-spin polarization are decoupled and have a vanishingly small transition amplitude. The two observable transitions are then determined by $|\Delta M_\mu| = 1$ and $\Delta M_e = 0$.

II. EXPERIMENTAL SETUP

The experiments were performed at SIN (Schweizerisches Institut für Nuklearforschung). The high muon flux of the superconducting muon channel allowed measurements with very high statistics. A usual μSR setup[1] with two positron counters was used, one counter in the beam direction and the other perpendicular to it.

The Ge samples were undoped and had a specified resistivity $\rho \geq 50$ Ωcm, corresponding to an electrically active impurity content of about $10^{13}/\text{cm}^3$. Single crystals of about 30 g and cylindrical shape were used. The targets were cooled in a thin window He flow cryostat. In each run 12–18 million events were accumulated.

III. RESULTS AND DISCUSSION

A. Anomalous muonium

In order to search for the anomalous muonium state in Ge, measurements were performed in strong transversal magnetic fields. The target temperature was 10 K. Figure 1 shows Fourier transforms of runs with $B = 0.45$ T and $B = 0.52$ T and the field axis ap-

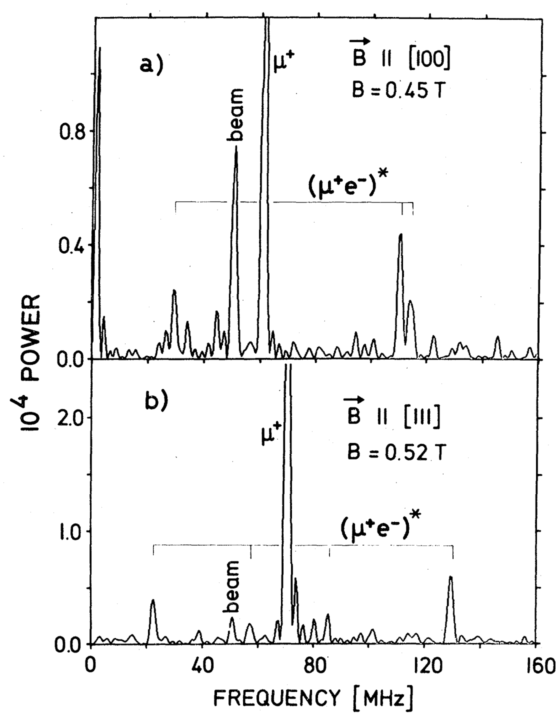

FIG. 1. Fourier spectra of two typical runs with an external field $B = 0.45$ T, approximately parallel to the [100] axis (a) and $B = 0.52$ T, approximately parallel to the [111] axis (b). Signals from the anomalous muonium in Ge are indicated by $(\mu^+e^-)^*$. The lines denoted μ^+ correspond to the Larmor frequency of muons in diamagnetic environment in the target and in the cryostat walls, respectively. The lines at 50 MHz are background signals, caused by the pulsed structure of the beam.

proximately parallel to the [100] and [111] direction of the crystal, respectively. The misalignment was 3° for the [100] and 7.5° for the [111] direction. Besides the strong lines from the Larmor precession of muons in a diamagnetic environment labeled μ^+ and the peaks at 50.6 MHz from the cyclotron beam, additional lines can be seen around 110 MHz in Fig. 1(a) and at 23 and 130 MHz in Fig. 1(b), while less pronounced peaks appear at 31 MHz [Fig. 1(a)] and at 57 and 85 MHz [Fig. 1(b)]. These lines are interpreted as being due to the anomalous muonium state $(\mu^+e^-)^*$ in Ge. The frequencies are plotted as a function of the magnetic field in Fig. 2. The dashed lines correspond to the Larmor frequency of the free muon. The solid lines are theoretical curves calculated from the anisotropic Hamiltonian (2) with fitted parameters $A_\perp$ and $A_\parallel$. From the best fit the following values are obtained:

$$A_\perp/h = 130.7 \pm 1.0 \text{ MHz},$$

$$A_\parallel/h = 26.8 \pm 1.0 \text{ MHz} .$$

An exact [100] orientation was assumed for the data of Fig. 2(a) whereas the misalignment of 7.5° was taken into account explicitly for the [111] orientation [Fig. 2(b)]. The different angles between the field and the symmetry axes, corresponding to one of the four equivalent [111] directions, are noted on the curves.

The results indicate that the anomalous muonium states in Si and Ge are quite similar. Both states exhibit the same symmetry. The anisotropy of the hyperfine interaction, measured by the ratio $A_\parallel/A_\perp$, is almost equal ($A_\parallel/A_\perp = 0.19$ for Si and 0.20 for Ge). The absolute value of the hyperfine constants are about 40% larger for Ge than for Si. As in Si the lifetime of the $(\mu^+e^-)^*$ signals in Ge is of the order of 1 μs. However, remarkable differences exist: (i) The amplitudes of the $(\mu^+e^-)^*$ signals in Ge are smaller by about a factor of 2 than those observed in

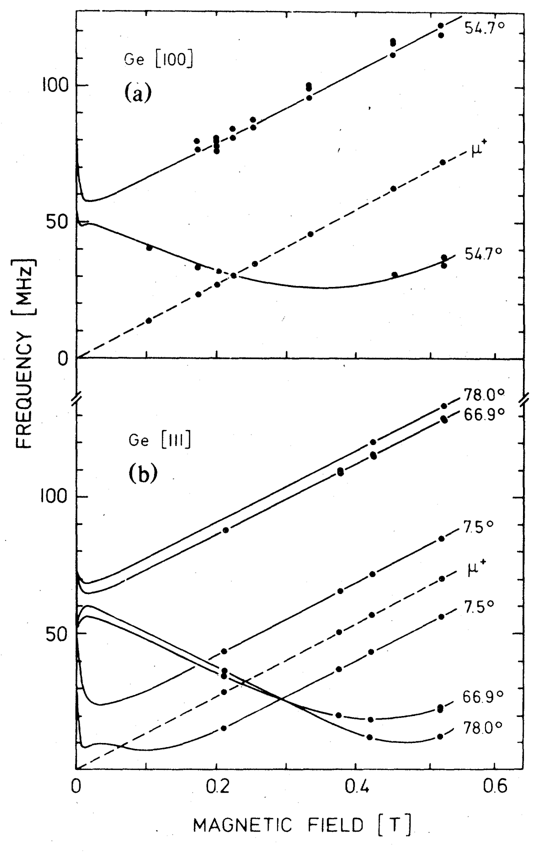

FIG. 2. Experimentally observed frequencies (points) as a function of the external field. The field direction was parallel to the [100] axis with a misalignment of 3° (a) and parallel to the [111] axis with a misalignment of 7.5 ° (b). The solid lines are calculated from Eq. (2) with fitted parameters $A_\perp$, $A_\parallel$. The angles θ, formed by the symmetry axes with the external field, are given on the right-hand side. The dashed lines correspond to the Larmor frequency of free muons.

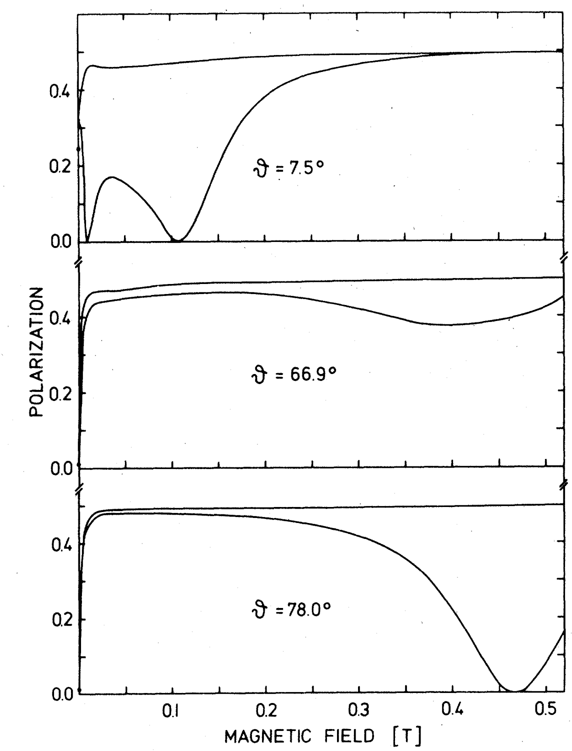

FIG. 3. Calculated amplitudes of $(\mu^+e^-)^*$ for a counter in direction of the initial polarization as a function of the external field. The crystal orientation corresponds to that of the data of Fig. 2(b). The larger polarization for a given angle θ corresponds always to the larger frequency in Fig. 2(b). The sum has been normalized to unity. The missing part for $B \gtrsim 0.005$ T is time independent.

Si under comparable conditions. (ii) In contrast to Si no signals from $(\mu^+e^-)^*$ could be detected in Ge below 0.1 T.

The disappearance of the $(\mu^+e^-)^*$ lines at low fields is not understandable on the basis of the Hamiltonian (2). The calculated amplitudes for a positron telescope in beam direction are shown in Fig. 3. The same crystal orientation as for the data of Fig. 2(b) is assumed. As can be seen in Fig. 3, the theoretical amplitudes at, say, 20 mT are partly the same or even larger than at strong fields but no frequencies corresponding to the anomalous muonium were observed. This is in contrast to Si where at low fields, a variety of signals were found.[4,9]

B. Normal muonium, hyperfine constant

The normal muonium in Ge was studied in the temperature range between 6 and 81 K. The Fourier transform of a measurement at an external field of 20 mT (Fig. 4) shows clearly the two precession frequencies ν_{12} and ν_{23} corresponding to the energy splitting in the triplet $F=1$ state of muonium. They are given by

$$h\nu_{12}=\tfrac{1}{2}\{A+(g_e\mu_B+g_\mu\mu_\mu)B-[A^2+(g_e\mu_B-g_\mu\mu_\mu)^2B^2]^{1/2}\},$$
$$h\nu_{23}=\tfrac{1}{2}\{-A+(g_e\mu_B+g_\mu\mu_\mu)B+[A^2+(g_e\mu_B-g_\mu\mu_\mu)^2B^2]^{1/2}\}. \tag{3}$$

For an accurate measurement of the hyperfine constant it is of advantage to use fields as high as allowed by the time resolution of the apparatus. Therefore most of the experiments were performed at 20 mT. The data were fitted by the following function:

$$N(t)=N_0e^{-t/\tau_\mu}\{1-a_\mu e^{-\lambda_\mu t}\cos(\omega_\mu t+\phi_\mu)-e^{-\lambda t}[a_{12}\cos(\omega_{12}+\phi)+a_{23}\cos(\omega_{23}t+\phi)]\}+b,$$
$$\omega=2\pi\nu. \tag{4}$$

The first cosine term describes the μ^+ component while the other terms refer to the two precession frequencies of μ^+e^-. A common relaxation rate λ for both μ^+e^- signals was assumed. λ_μ is the relaxation rate for the free muon component. From the measured frequencies, a unique hyperfine constant A can be extracted from Eq. (4), corresponding to the isotropic Hamiltonian (1). In Fig. 5, the results are plotted as a function of temperature. Within the errors, there is no temperature dependence. The weighted average is

$$A(\mathrm{Ge})/h=2361\pm3\,\mathrm{MHz},$$
$$A(\mathrm{Ge})A(\mathrm{vac})=0.5290\pm0.0007. \tag{5}$$

The errors quoted include the statistical errors and a systematic error due to the time calibration. This value of A(Ge) is considerably lower than that reported in Ref. 5 but it is in agreement with recent experiments on Ge samples with different doping concentrations.[10] There is no evidence for an additional anisotropic term in the Hamiltonian describing normal muonium, an upper limit for a deviation from isotropy being 1%.

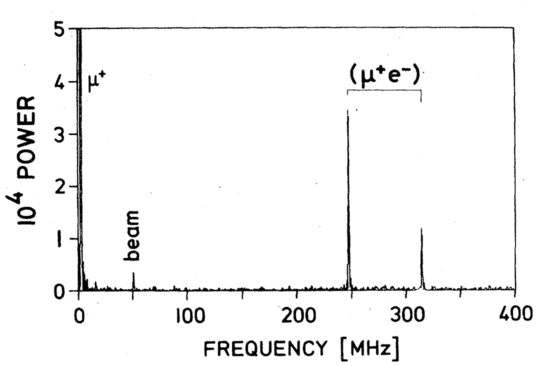

FIG. 4. Fourier spectrum of a run at 13 K and with an external field of 0.02 T. The two frequencies of normal muonium are denoted by μ^+e^- and the diamagnetic compound by μ^+. The line at 50 MHz is a background signal from the pulsed beam.

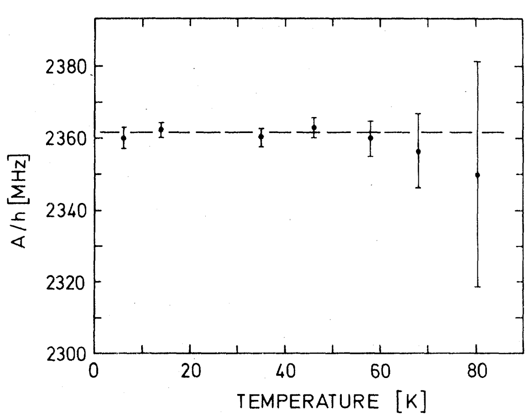

FIG. 5. Measured hyperfine constant A of normal muonium in Ge as a function of temperature. The dashed line is the weighted mean value of the plotted data points.

C. Normal muonium, relaxation rate

The relaxation rate λ of the μ^+e^- signals plotted in Fig. 6 shows a sharp rise above about 50 K. A fit of these data for $T > 35$ K to an Arrhenius law gives an activation energy $E_a = 14$ meV. This is in the range of the ionization energies E_0 of usual donors in Ge ($E_0 \simeq 9 - 13$ meV) and is much lower than the band gap $E_g \approx 700$ meV. Therefore on the basis of the present experiment a relaxation mechanism which involves thermally activated impurity electrons (or holes) seems plausible. The theory of muonium depolarization, developed by Ivanter and Smilga,[11] explains the muon spin relaxation by an incoherent spin flip at the muonium electron with mean frequency ν. For our case of weak relaxation, λ is equal to $\frac{3}{2}\nu$. Adopting this model, the relaxation may be caused by the scattering of charge carriers at the muonium atom with a mutual spin flip of the involved electrons.[12] Since the electron concentration n_e in the conduction band is small, it would follow that $\lambda \sim \nu \sim n_e$. However, other mechanisms leading to a relaxation of the muon spin should be considered also, e.g., diffusion of muonium to inequivalent sites, chemical reactions leading to diamagnetic compounds, phonon induced relaxation or thermal ionization of muonium. The latter mechanism would imply that muonium is a shallow donor in contrast to earlier suggestions. Measurements with different doping concentrations should give an answer to these questions.

In Table I we give the probabilities of the observed muon states in the present experiment. The formation probability for normal muonium was taken from the low-field experiment, which was analyzed according to Eq. (4). The value of $(\mu^+e^-)^*$ was derived from the Fourier spectra of the measurements with high fields. In both cases the amplitudes of the unobserved frequencies or time-independent parts were taken into account. "Cryostat" means the fraction of muons stopped in the cryostat walls. The value of μ^+ does not include this part.

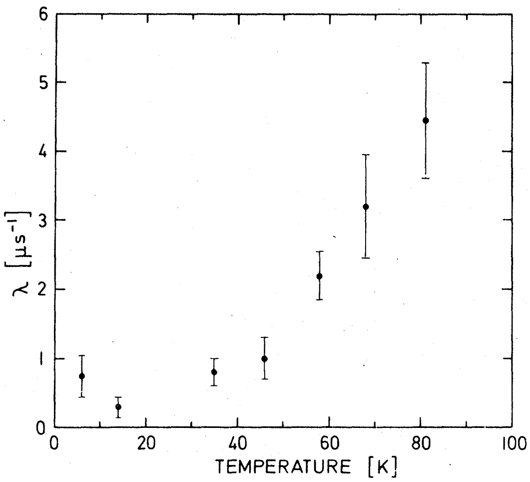

FIG. 6. Experimentally observed relaxation rates λ of normal muonium in Ge as a function of temperature.

IV. MICROSCOPIC MODELS

Several models have been proposed for the anomalous muonium $(\mu^+e^-)^*$ in Si.[4] Since a similar state has been found in Ge, these models should apply also to this case.

One model is based on the diamond-type lattice of Ge and Si. There exist two natural interstitial sites, one site with tetrahedral and one site with hexagonal local symmetry.[13] The possibility that these sites are occupied by muonium has been considered in Ref. 14. Assuming that the distortion of the electron wave function reflects the local symmetry of the site, the dipolar part of the hyperfine interaction leads to an anisotropic spin Hamiltonian of the form of Eq. (2) for the hexagonal site, whereas an isotropic spin-Hamiltonian results for the tetrahedral site. A possible explanation is thus given by assigning the normal muonium state to muons trapped at the tetrahedral site and the anomalous to muons at the hexagonal site.

However, extended Hückel theory calculations for a model crystal of 30–40 Si atoms gave the result that for hydrogen the energetically stable position is the tetrahedral site whereas the hexagonal site is only a saddle point.[15] Although it is questionable whether this result can be applied to muonium in a real crystal, it nevertheless casts some doubts on the preceding explanation.

Recently, a direct determination of the lattice location of deuterium in Si has been reported by Picraux and Vook.[16] They introduced deuterium in single

TABLE I. Formation probability of muonium states in Ge at $T = 10$ K.

	μ^+	μ^+e^-	$(\mu^+e^-)^*$	Cryostat	Total
%	10 ± 5	35 ± 5	25 ± 10	7 ± 3	77 ± 23

crystal Si by ion implantation and subsequently determined its location by ion channeling. As a result, they give an interstitial site on a [111] axis, 1.6 Å from a Si atom in the antibonding direction. The specific nature of the silicon deuterium bonding, however, is not known.

A further model is based on the fact, that during the slowing down process of a fast muon, a large number of electron-hole pairs are produced. At the end of its range, the muon may capture an electron and form a normal muonium, or fail to do this and contribute to the μ^+ component, or interact with a nearby hole[3] giving rise to the anomalous muonium. In this model, $(\mu^+e^-)^*$ is considered as a double charged center, consisting of a muon and a broken Ge-Ge bond. This state is paramagnetic. The electron wave function is expected to be a mixture of a Ge orbital and a muonium orbital, which may strongly differ from spherical symmetry with respect to the muon site.

V. CONCLUSION

The discovery of an anomalous muonium state in Ge has removed an apparent difference between Si and Ge. The field dependence of the observed frequencies is in both cases well described by the spin Hamiltonian (2), but unexplained differences remain: The amplitudes of the $(\mu^+e^-)^*$ frequencies in Ge are generally smaller than in Si and show an unexplained field dependence at low fields. It is suggested that in Ge an additional interaction is present, which can be decoupled at higher fields. The nature of this interaction is unknown. For the normal muonium in Ge new precise data are presented. The measurement of the relaxation rate provides a quantitative basis for further considerations on the relaxation mechanism in semiconductors. However, it seems that additional experiments on differently doped Ge crystals and similar data for Si are required for an understanding of the underlying processes.

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[1]J. H. Brewer, K. M. Crowe, F. N. Gygax, and A. Schenck, in *Muon Physics Vol. III: Chemistry and Solids,* edited by V. W. Hughes and C. S. Wu (Academic, New York, 1975).

[2]A. Schenck, in *Nuclear and Particle Physics at Intermediate Energies,* edited by J. B. Warren (Plenum, New York, 1976).

[3]J. H. Brewer, K. M. Crowe, F. N. Gygax, R. F. Johnson, B. D. Patterson, D. G. Fleming, and A. Schenck, Phys. Rev. Lett. 31, 143 (1973).

[4]B. D. Patterson, W. Kündig, P. F. Meier, F. Waldner, H. Graf, E. Recknagel, A. Weidinger, Th. Wichert, and A. Hintermann, Phys. Rev. Lett. 40, 1347 (1978).

[5]I. I. Gurevich, I. G. Ivanter, E. A. Melesko, B. A. Nikol'skii, V. S. Roganov, V. I. Selivanov, V. P. Smilga, B. V. Sokolov, and V. D. Shestakov, Sov. Phys. JETP 33, 253 (1971).

[6]G. Feher, R. Prepost, and A. M. Sachs, Phys. Rev. Lett. 5, 515 (1960).

[7]B. Eisenstein, R. Prepost, and A. M. Sachs, Phys. Rev. 142, 217 (1966).

[8]J. Shy-Yih Wang and C. Kittel, Phys. Rev. B 7, 713 (1973).

[9]C. Boekema, W. Kündig, P. F. Meier, W. Reichart, K. Rüegg, H. Graf, A. Hintermann, and B. D. Patterson, Hyper. Inter. 6, 167 (1979).

[10]H. Graf *et al.* (unpublished).

[11]I. G. Ivanter and V. P. Smilga, Sov. Phys. JETP 27, 301 (1968).

[12]W. E. Fischer, Helv. Phys. Acta 49, 629 (1976).

[13]K. Weiser, Phys. Rev. 126, 1427 (1962).

[14]Y. M. Belousov, V. N. Gorelkin, and V. P. Smilga, Sov. Phys. JETP 47, 331 (1978).

[15]V. A. Singh, C. Weigel, J. W. V. Corbett, and L. M. Roth, Phys. Status Solidi 81, 637 (1977).

[16]S. T. Picraux and F. L. Vook, Phys. Rev. B 18, 2078 (1978).