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Temperature dependence of the hyperfine parameters of anomalous muonium in germanium

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The anomalous-muonium hyperfine interaction in germanium has been measured as a function of temperature between 5 and 100 K. It was found that the component perpendicular to the defect axis decreases while the component parallel to the axis increases as the temperature increases. Both effects are a result of the interaction of anomalous muonium with the germanium-host phonons. The temperature dependences of the anomalous-muonium hyperfine interaction in diamond, silicon, and germanium are compared.

I. INTRODUCTION

Muon spin rotation (μSR) spectra of the three group-IV elements, diamond, silicon, and germanium, all display two muoniumlike centers. One resembles the free muonium atom in that a large isotropic hyperfine interaction is observed.[1] However, this normal muonium Mu has a hyperfine splitting less than that of free muonium by a factor of about 2.2 in silicon, 1.9 in germanium, and 1.2 in diamond. Another more unusual center called anomalous muonium, Mu* is also obesrved.[1-4] Anomalous muonium has axial symmetry about a $\langle 111 \rangle$ axis, the hyperfine interaction is very anisotropic, and the average interaction is more than an order of magnitude weaker than for free muonium. The spin Hamiltonian including an axially symmetric electronic g tensor is given by

$$\mathcal{H}=g_{||}\mu_B H_z S_z+g_{\perp}\mu_B(H_x S_x+H_y S_y)$$

$$-g_\mu\mu_\mu\vec{\mathrm{H}}\cdot\vec{\mathrm{I}}+A_{||}S_z I_z+A_{\perp}(S_x I_x+S_y I_y)\ .$$

The temperature dependence of the two hyperfine parameters, $A_{||}$ and $A_{\perp}$, of Mu* in silicon (for which it is known[2] that $A_{||}/A_{\perp}>0$) were measured by Blazey *et al.*[5] They found that both $A_{||}$ and $A_{\perp}$ decreased as the temperature increased. Although the change was somewhat larger than normally encountered for paramagnetic centers in solids, it was not unusual. The temperature dependence implied that phonons with energies typical for the host lattice were responsible. Measurements on diamond ($A_{||}/A_{\perp}<0$) by Holzschuh *et al.*[4] showed that while $A_{\perp}$ decreased, $A_{||}$ increased with increasing temperature. Again, the temperature dependence was found to be due to interaction with the host phonons. Here, we report measurements on the temperature dependence of $A_{||}$ and $A_{\perp}$ for germanium ($A_{||}/A_{\perp}>0$). Like diamond, but unlike silicon, it was found that $A_{\perp}$ decreases while $A_{||}$ increases with increasing temperature.

II. EXPERIMENT

A germanium crystal of the highest purity currently available[6] was measured in the μE4 area at the Swiss Insitute for Nuclear Research. The crystal was mounted in a He-gas-flow cryostat between Helmholtz coils providing a 2000-gauss magnetic field. The temperature was measured with a carbon-resistance thermometer and a copper-constantan thermocouple. At each temperature, time-differential transverse-field muon spin rotation data were gathered in four histograms from which the precession frequencies and their relaxation rates were extracted by multifrequency fits. Two sets of data were taken, one with the applied field approximately parallel to $\langle 111 \rangle$ to determine $A_{||}(T)$, and another set with the applied field almost parallel to $\langle 110 \rangle$ where $A_{\perp}(T)$ was determined.

When the field is parallel to a $\langle 111 \rangle$ axis, it makes an angle of 0° with respect to the symmetry axis of one of the Mu* centers, and 70.5° with

respect to the other three Mu* centers. The difference between the two μSR frequencies of the 0° center at high fields is then equal to $A_{||}$, as shown earlier[5]:

$$A_{||}=h\nu_{21}-h\nu_{43} .$$

In this case, the 0° lines have frequencies of approximately 13.9 and 41.2 MHz, while the 70.5° centers have lines near 36.5 and 88.0 MHz.

Similarly,[5] the two Mu* centers whose axes are perpendicular to the field when it is parallel to a ⟨110⟩ axis yield $A_{\perp}$,

$$A_{\perp}=h\nu_{21}+h\nu_{43} .$$

When the field is along a ⟨110⟩ direction, the 90° centers have lines at about 38.6 and 92.4 MHz, and the other two centers at 35.3° have lines at approximately 24.5 and 62.7 MHz. As will be discussed in Sec. III, the measured A values were corrected for small misalignments of the crystal in the external magnetic field.

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the components $A_{||}$ and $A_{\perp}$ of the Mu* hyperfine interaction. If we assume that $A_{\perp}$ is positive, as is usually done in the literature on anomalous muonium and will be discussed later, then it is observed to decrease 1.4% over the temperature range 0–100 K. The parallel component $A_{||}$ shows a 2% increase over the same temperature range.

We can discount the possibility that lattice-expansion effects are responsible for the changes observed, because of the strongly nonmonotonic temperature dependence[7] of the germanium lattice constants in the temperature range investigated, which

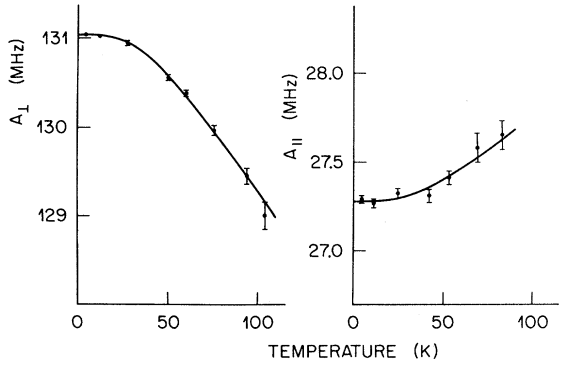

FIG. 1. Temperature dependence of parallel $A_{||}$ and perpendicular $A_{\perp}$ components of the hyperfine interaction tensor of anomalous muonium in germanium. The solid lines show the fit of the Debye model to the data points.

contrasts with the monotonic dependences of $A_{\perp}(T)$ and $A_{||}(T)$. We thus ascribe the temperature dependence in Fig. 1 to the spin-phonon interaction. If interaction with a Debye phonon spectrum is assumed, then in the long-wavelength limit[8]

$$A(T)=A(0)\left[1-C\frac{T^4}{\Theta_D^4}\int_0^{\Theta_D/T}\frac{x^3}{e^x-1}dx\right],$$

where C is a constant and Θ_D is the Debye temperature.

Interaction with a single Einstein oscillator gives[9]

$$A(t)=A(0)\left[1-C\left[\coth\frac{h\nu}{2kT}-1\right]\right],$$

where $h\nu$ is the energy of the interacting phonon mode. Both of these models were found to fit the temperature variation of $A_{||}$ and $A_{\perp}$ in silicon, while the Debye model was found to give a better fit to $A_{||}$ and $A_{\perp}$ in diamond. In this study of germanium, a better fit was found for the Debye model, provided the Debye temperature was allowed to vary to an effective Debye temperature Θ_D'. This was also found necessary in analyzing the silicon results,[5] but not the diamond results,[4] and is probably related to the fact that the Debye temperature varies considerably[10] over the temperature range of the silicon and germanium measurements, but varies only little over the temperature range where there is significant change of $A_{||}$ and $A_{\perp}$ in diamond.

The parameters derived for the best fit of the germanium results to the Debye model are

$$A_{\perp}(0)=131.037\pm0.009 \quad (\chi^2/\nu=1.03) ,$$

$$A_{||}(0)=27.279\pm0.013 \quad (\chi^2/\nu=1.02),$$

$$C_{\perp}=0.113\pm0.020 ,$$

$$C_{||}=-0.149\pm0.024,$$

$$\Theta_D'=152\pm14 ,$$

where $A_{\perp}(0)$ and $A_{||}(0)$ are in units of MHz, and Θ_D' is in K. The effective Debye temperature is less than half the literature value[11] of 360 K.

On the other hand, the parameters providing the best fit to the coth law are

$$A_{\perp}(0)=131.035\pm0.011 \quad (\chi^2/\nu=1.41) ,$$

$$A_{||}(0)=27.280\pm0.013 \quad (\chi^2/\nu=1.06) ,$$

$$h\nu/k=104\pm10,$$

$$C_{\perp}=0.012\pm0.002,$$

$$C_{||}=-0.016\pm0.003,$$

where $A_{\perp}(0)$ and $A_{||}(0)$ are in units of MHz, and $h\nu/k$ is in K.

Since the determination of $A_\perp$ from the data of Fig. 1 is much more accurate than that of $A_{||}$, the characteristic phonon temperatures, Θ'_D and $h\nu/k$ of both models were obtained from fits to the $A_\perp(T)$ data, and then held fixed for the fits to determine the parameters of the $A_{||}$ results. The agreement between the $T=0$ K hyperfine interaction parameters of both models is very good, but the reduced chi squared χ^2/ν for the Debye model is somewhat lower. We take the quality of these fits and the fact that the fitted energies $k\Theta'_D$ and $h\nu$ are typical of phonons as evidence that, as with diamond and silicon, it is interaction with host phonons that causes the temperature dependence of the Mu* hyperfine interaction.

The data obtained with the field approximately parallel to ⟨111⟩ showed that the lines from the three centers at about 70.5° were split into two, thus indicating a misalignment. By fitting all of the lines observed to the spin Hamiltonian, the tilt of the field from the ⟨111⟩ direction was determined to be 0.95° toward the closest ⟨110⟩ direction in the {110} plane. The correction to the measured quantity is given by the relationship valid for high field and small angle θ between the field and the symmetry axis,

$$h\nu_{21}-h\nu_{43}=A_{||}+\left[A_{||}\frac{\Delta g}{g_0}-\frac{1}{4}\frac{A_\perp-A_{||}}{(g_\mu\mu_\mu H)^2-\frac{1}{4}A_{||}^2}\left[\frac{1}{2}A_{||}(A_\perp+A_{||})-4(g_\mu\mu_\mu H)^2-\frac{A_{||}A_\perp g_\mu\mu_\mu}{g_0\mu_B}\right]\right]\theta^2 ,$$

where $g_0=\frac{1}{3}(g_{||}+2g_\perp)$ and $\Delta g=g_{||}-g_\perp$. The value of $A_{||}$ was obtained by subtracting 0.010 MHz from the uncorrected value.

No splitting of the lines due to the two centers at 35.3° was observed in the data taken with the field approximately parallel to ⟨110⟩. This observation implies that the field was in a {100} plane. Fitting all the lines observed allows an estimate of the misalignment in this plane. This procedure gave a good fit for perfect alignment, although a misalignment of up to about 1.4° would not have altered the quality of the fit appreciably. We increased the uncertainty to allow for this. The final values for the hyperfine parameters in germanium extrapolated to zero temperature are then (in MHz)

$$A_\perp(0)=131.037\pm0.034,$$

$$A_{||}(0)=27.269\pm0.013 .$$

In making these misalignment corrections, we found an error in the corrections applied to the $A_{||}$ data in silicon.[5] The correct values for silicon, based on the Debye-model fit extrapolated to $T=0$, are (in MHz)

$$A_\perp(0)=92.59\pm0.05,$$

$$A_{||}(0)=16.819\pm0.011 .$$

The corrected values of silicon together with the results for diamond and germanium are shown in Table I. A physically more useful description of the

TABLE I. Hyperfine parameters, coupling constants, and Debye temperatures describing the temperature dependence of the anomalous muonium hyperfine interaction in diamond, silicon, and germanium assuming interaction with a Debye phonon spectrum. The energies of the single Einstein oscillators $h\nu/k$ used in the coth law are included. The values taken from Refs. 4 and 5 have been doubled as a factor of 2 was omitted in these papers.

	Diamond	Silicon	Germanium
$A_{||}(0)$ (MHz)	−167.983(57)	16.819(11)	27.269(13)
$A_\perp(0)$ (MHz)	392.586(55)	92.59(5)	131.037(34)
$C_{||}$	0.727(36)	0.160(34)	−0.149(24)
$C_\perp$	0.379(19)	0.371(148)	0.113(20)
Θ'_D (K)	1902(51)	425(66)	152(14)
Θ_D (K) (Ref. 11)	1860	625	360
$h\nu/k$	1306(38)	520(16)	104(10)
$A_s(0)$ (MHz)	205.730(41)	67.333(34)	96.448(23)
$A_p(0)$ (MHz)	−186.856(26)	−25.257(17)	−34.589(12)
C_s	0.284(26)	0.353(136)	0.088(18)
C_p	0.483(17)	0.418(181)	0.182(26)
$A_s(0)C_s/\Theta'^4_D$ (MHz K^{-4})	$4.46(63)\times10^{-12}$	$7.30(534)\times10^{-10}$	$1.59(67)\times10^{-8}$
$A_p(0)C_p/\Theta'^4_D$ (MHz K^{-4})	$-6.90(78)\times10^{-12}$	$-3.25(246)\times10^{-10}$	$-1.18(47)\times10^{-8}$

hyperfine interaction results if it is written in terms of the isotropic or contact interaction A_s and the axial dipolar interaction or A_p. (These contributions arise from s and p orbitals, respectively, if the unpaired electron spin is in an orbital which is s- and p-like on the μ^+.) In terms of $A_{||}$ and $A_\perp$, they are[12]

$$A_s=\tfrac{1}{3}(A_{||}+2A_\perp),\quad A_p=\tfrac{1}{3}(A_{||}-A_\perp)\ .$$

Inserting the $T=0$ K values of $A_{||}$ and $A_\perp$ of germanium yields (in MHz)

$$A_s(0)=96.448\pm0.023,$$

$$A_p(0)=-34.589\pm0.012\ .$$

These values are compared with those of diamond and silicon in Table I.

The above equations may be used to determine the temperature dependence of A_s and A_p from the fitted $A_{||}(T)$ and $A_\perp(T)$ for diamond, silicon, and germanium. The results of such a decomposition of the hyperfine interaction plotted against temperature are shown in Fig. 2, and the parameters are given in Table I. In all cases, there is a decrease in the magnitude of both s and p components of the hyperfine interaction with increasing temperature, with the relative change in A_p being more rapid than for A_s. For a given crystal, the derivatives of A_s and A_p with temperature are proportional to the quantities $A_s(0)C_s/\Theta_D'^4$ and $A_p(0)C_p/\Theta_D'^4$, the last two entries in Table I, respectively. These two quantities are also a measure of the spin-phonon coupling which leads to the temperature dependence.[13] The coupling in germanium is approximately 30 times larger than in silicon, which in turn is about 80 times larger than for diamond.

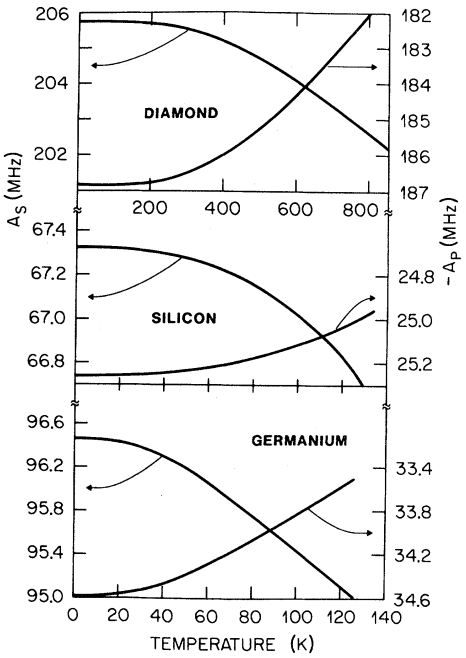

FIG. 2. Temperature variation of the isotropic A_s and anisotropic A_p components of the anomalous muonium hyperfine interaction in diamond, silicon, and germanium derived from the fits of the Debye model to $A_{||}$ and $A_\perp$.

In much of the literature, it is implicitly assumed that the overall signs of the hyperfine parameters are such that $A_\perp$ is positive for Mu* in diamond, silicon, and germanium. (There is a suggestion that $A_\perp>0$ for diamond in the high-temperature studies of the conversion of Mu to Mu*.[14]) If this assumption is made, it results in the isotropic component A_s being positive and in the anisotropic component A_p being negative for all three crystals. A negative value of A_p implies an electron spin density primarily in the plane perpendicular to the Mu* symmetry axis, and the origin of the positive A_s could then be overlap effects, although it is unclear as to why they should be so small.

It is implausible for any one of the three crystals to have the sign of $A_\perp$ opposite to those of the others, for in that case, A_s, A_p, C_s, and C_p would also have signs opposite to those of the other two crystals. However, the signs of these parameters would be the same for all three crystals, if $A_\perp$ were negative for all. This would imply $A_s<0$ and $A_p>0$. Such a negative isotropic hyperfine interaction could result, if two spin-paired electrons which were s-like on the muon were negatively spin polarized by exchange with the unpaired electron which would have to have negligible contact interaction with the muon spin. (A positive A_p would then imply an electron spin density primarily near the $\langle 111\rangle$ symmetry axis of Mu*.) These conditions would be so unusual that this possibility is unlikely.

The depolarization rate λ of Mu* in germanium is shown in Fig. 3 as a function of temperature for the

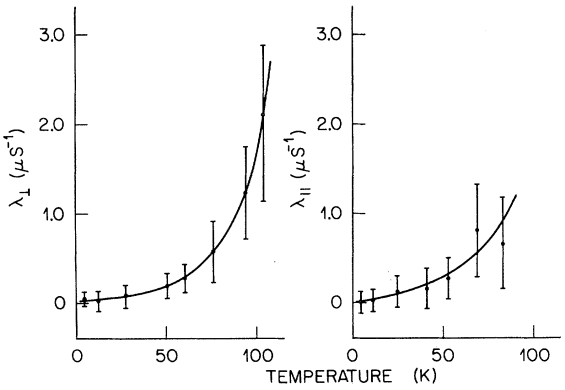

FIG. 3. Temperature dependence of the depolarization of anomalous muonium in germanium with the field parallel and perpendicular to the Mu* symmetry axis. The solid lines are only guides for the eye.

fields perpendicular and parallel to the Mu* symmetry axis. It is seen to increase rapidly with temperature above 80 K. A similar rapid increase was observed for silicon[5] near 120 K. On the other hand, no appreciable increase in the zero-field linewidths was observed for Mu* in diamond up to 1000 K.

An Arrhenius plot of the depolarization rate in germanium gives an activation energy of 26 meV for the rapid rise above 60 K. This may be compared to 110 meV found in silicon.[5] The increased depolarization in silicon could not be attributed to free carriers, as the results do not vary with crystals of different conductivity. The silicon results are in fact consistent with a Raman process for the depolarization rate causing a T^9 temperature variation for the $S=\frac{1}{2}$ system. A log-log plot of the depolarization-rate temperature dependence in germanium shows a slope of 3.7 and is not, therefore, consistent with a phonon-induced relaxation via a Raman process. Weidinger *et al.*[15] have reported a variation of the temperature dependence of the depolarization rate in germanium that is dependent upon the crystal doping. The results reported here are very similar to those found by these authors for an undoped crystal, and they indicate that the disappearance of Mu* at high temperature is a result of an increasing relaxation rate and not a decreasing amplitude.

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