Evidence for Magnetic-Field-Dependent Electric-Field Gradients in Bi from Muon-Spin-Relaxation Measurements

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The field dependence of the anisotropic second moment of the nuclear dipolar field distribution in rhombohedral Bi at 11 K observed by muon-spin relaxation in a single-crystal sample is in complete contrast to the results of well established calculations. A phenomenological model of an electric field gradient rotated by the external magnetic field allows description of the data; its physical justification, however, is not clear.

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The broadening of magnetic resonance lines of spins in solids due to purely dipolar coupling is a well-known and understood phenomenon in nuclear magnetic resonance (NMR) [1]. The essential parameter describing the linewidth is the second moment M_2 of the dipolar field distribution which is given by Van Vleck's formula [2] [see Eq. (1)]. In the Van Vleck theory the spins are assumed to be subject, except for their dipolar coupling, only to the Zeeman interaction in the external field $B_{\rm ext}$. M_2 is then independent of the strength of $B_{\rm ext}$, a prediction that has never come into conflict with NMR results, which were usually obtained in strong external fields. Later, field-dependent M_2 were discovered in muon-spin-rotation (μSR) experiments (first in Cu [3]), where $B_{\rm ext}$ is generally smaller than in NMR experiments. This led to an extension of the Van Vleck theory by Hartmann [4] who took into account the electric quadrupolar interaction of nuclear spins. His model could until now explain all M_2 data observed by μSR. In this paper we report on the observation of a new type of field dependence of M_2 for μ^+ implanted in the semimetal Bi. The effect cannot be described by Hartmann's original scheme and calls for yet another extension of the basic assumptions entering into such theories.

In the Van Vleck theory the second moment of the essentially Gaussian distribution of nuclear dipolar fields—in our case sensed by the spin precession frequencies of positive muons implanted at an interstital site in bismuth—is given by

$$M_2=\gamma_\mu^2\sum_i\langle(H_{i,z}^{\rm dip})^2\rangle_{\rm av}=\gamma_\mu^2\gamma_I^2\hbar^2\sum_i\langle\langle I_{z,i}^2\rangle\rangle_{\rm av}\frac{(3\cos^2\theta_i-1)^2}{r_i^6}$$

$$=\frac{1}{3}I(I+1)\gamma_\mu^2\gamma_I^2\hbar^2\sum_i\frac{(3\cos^2\theta_i-1)^2}{r_i^6}. \qquad (1)$$

$$M_2^Q=\hbar^2\gamma_\mu^2\gamma_I^2\sum_i\left\langle\left[\frac{\langle I_{z,i}\rangle(1-3\cos^2\theta_i)}{r_i^3}-\frac{3\langle\mathbf{I}_{x,i}\rangle\cdot\mathbf{r}_i\cos\theta_i}{r_i^4}\right]^2\right\rangle_{\rm av}. \qquad (3)$$

The expectation values $\langle I_{z,i}\rangle$ and $\langle I_{x,i}\rangle$ have to be calculated for each nucleus i from a diagonalization of the full nuclear hyperfine Hamiltonian which in the present case is given by [1]

$$H_{\rm hf}^{(i)}=\frac{eV_{z^*z^*}^{(i)}Q}{4I(2I-1)}[3I_{z^*}^2-I(I+1)+\tfrac{1}{2}\eta_i(I_{+^*}^2-I_{-^*}^2)]+\gamma_I\mathbf{I}\cdot\mathbf{H}_{\rm ext}. \qquad (4)$$

$H_{i,z}^{\rm dip}$ is the static component parallel to the external field $\mathbf{B}_{\rm ext}$ of the dipolar field at the muon site produced by the ith nucleus with spin I, and the average, $\langle\,\rangle_{\rm av}$, is taken over all Zeeman states, and $\langle\,\rangle$ without a subscript refers to an expectation value. The sum runs over all nuclei around the μ^+; r_i is the distance from the ith nucleus to the μ^+, θ_i denotes the angle between $\mathbf{r}_i$ and $\mathbf{B}_{\rm ext}$, and γ_μ and γ_I are the gyromagnetic ratios of the muon and the nuclei, respectively. The nuclear spins precess around $\mathbf{B}_{\rm ext}$ which therefore provides a convenient axis of quantization. The general angular dependence of M_2 for a μ^+ at an interstitial site with point-group symmetry D_{3d} in rhombohedral Bi can be expressed as [5]

$$M_2(\theta)=M_{2,\rm iso}^{VV}+AP_2^0(\cos\theta)+BP_4^0(\cos\theta)+CP_4^3(\cos\theta)\sin3\phi, \qquad (2)$$

where θ denotes the angle between the threefold c axis and $\mathbf{B}_{\rm ext}$, whereas ϕ is the azimuthal angle between the projection of $\mathbf{B}_{\rm ext}$ onto the basal plane normal to the c axis and a crystalline reference axis in the basal plane. $M_{2,\rm iso}^{VV}$ is the isotropic part of Eq. (1) and $P_l^m(\cos\theta)$ are normalized associated Legendre polynomials. A, B, and C are constants which can be calculated from lattice sums once the μ^+ site is chosen.

If now, as in Hartmann's theory [4], the nuclear spins are subject to an additional quadrupolar interaction, provided that the nuclei possess a quadrupolar moment Q, and that nonzero electric-field gradients (EFG) are present at the nuclear sites, the nuclear spin will no longer precess around $\mathbf{B}_{\rm ext}$ but around a new axis. The latter is determined by the combined effects of Zeeman and quadrupolar interaction. As a consequence the precessing nuclear spins not only have a static component along $B_{\rm ext}$, $\langle I_z\rangle$, but also a static component into a defined perpendicular direction, $\langle I_x\rangle$. M_2 can then be written as [6]

$V^{(i)}_{z^*z^*}$ is the EFG along a principal axis (z^*) of the gradient tensor at a given nucleus i. z^* may be different for different nuclei. The parameter $\eta_i = (V^{(i)}_{x^*x^*} - V^{(i)}_{y^*y^*})/V^{(i)}_{z^*z^*}$ is a measure of the deviation from an axially symmetric EFG. The ratio $\langle I_x\rangle/\langle I_z\rangle$ depends on the ratio of the Zeeman to the quadrupolar interaction energy, i.e., $\omega_Z/\omega_Q \equiv \gamma_I B_{\rm ext}/[eV_{z^*z^*}Q/4I(2I-1)\hbar]$. For a dominant Zeeman interaction ($\omega_Z/\omega_Q \geq 100$, high-field or Van Vleck limit),

$$\langle\langle I_x\rangle^2\rangle_{\rm av} = 0, \quad \langle\langle I_z\rangle^2\rangle_{\rm av} = I(I+1)/3 ,$$

and Eq. (3) reduces to Eq. (1). No general analytical expression for the angular dependence of $M_2^Q(\theta)$, analogous to Eq. (2), can be derived, but in the limit of dominant quadrupolar interaction, i.e., $\omega_Z/\omega_Q \ll 1$, it can be analytically shown that Eq. (3) assumes the form [7]

$$M_2^Q(\theta) = M_{2,\rm iso}^Q + DP_2^0(\cos\theta) , \qquad (5)$$

where θ is defined as for Eq. (2). Equation (5) is valid for arbitrary EFG tensors, including the case $\eta \neq 0$.

Equations (2) and (5) therefore represent the angular dependence of M_2 in the limits of very strong and very weak $B_{\rm ext}$, respectively.

Using previously obtained information from zero-field μSR measurements on the direction of the EFG at the nearest-neighbor Bi nuclei (which is directed along the axis connecting the μ^+ and a Bi neighbor, $\eta_i = 0$) and on the μ^+ site [6,8] (the latter is also inferred from cluster calculations [9]), $M_2(\theta)$ was calculated on the basis of Eq. (3). The results for different ω_Z/ω_Q are displayed in Fig. 1. For small ω_Z/ω_Q we notice the anticipated $\cos^2\theta$ dependence. It should be emphasized that the qualitative features of the curves in Fig. 1 do not depend on the chosen μ^+ site or the assumed directions of the EFGs. So Fig. 1 represents what we expected to find experimentally.

In our experiment using a spherical single-crystal sample of high purity (99.999%), $M_2(\theta)$ was determined from the Gaussian decay of the μ^+ precession signal. The relaxation rate σ is related to M_2 as $\sigma^2 = M_2/2$. By using the stroboscopic μSR technique [10] σ was determined for $B_{\rm ext} = 0.249$, 0.374, 0.498, and 0.747 T as a function of θ, and in part as a function of ϕ. Additional data at $B_{\rm ext} = 0.013$, 0.05, 0.90, and 1.06 T were obtained by the conventional time-differential μSR technique [10]. Above about 13 K the μ^+ starts to diffuse in pure Bi [6]. The present measurements were therefore all performed at $\sim$11 K, i.e., at a temperature at which the μ^+ can be considered immobile. The stroboscopic data are shown in Figs. 2 and 3. The results obtained by the time-differential method at small fields are very similar to the 0.249-T data and those at high fields are very similar to the 0.747-T data, respectively. The drastic field dependence seen in Figs. 2 and 3 is therefore confined to $0.25\ {\rm T} \lesssim B_{\rm ext} \lesssim 0.75$ T.

As can be seen from Figs. 2 and 3 the data are in principle well described by θ dependences of the type of Eq. (2). The field dependence of $M_2(\theta)$, however, is opposite to what is expected (see Fig. 1). While the high-field data follow approximately a $P_2^0(\cos\theta)$ dependence [corresponding to dominating quadrupole interaction, Eq. (5)], the low-field data are suggestive of a pure Van Vleck behavior [dominating Zeeman interaction, Eq. (2)] in view of the presence of sizable $P_4^0(\cos\theta)$ and $P_4^3(\cos\theta)$ terms. Moreover, the fact that the $P_4^3(\cos\theta)$ term has not disappeared for $\phi = 0°$ (see Fig. 3) shows that Eq. (2) is in fact

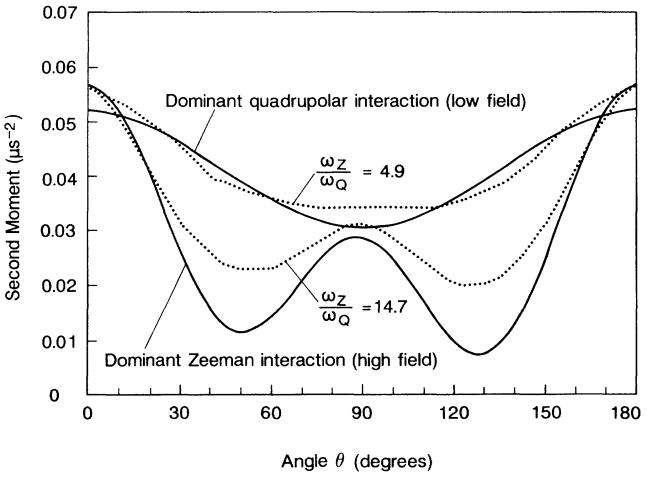

FIG. 1. Calculated orientational dependence of the second moment M_2 with respect to interstitial μ^+ in rhombohedral Bi [8] for different ratios of the Zeeman to the quadrupolar interaction frequency, ω_Z/ω_Q (see text for details). θ is the angle between $\mathbf{B}_{\rm ext}$ and the crystalline c axis. The azimuthal angle is set at $\phi = 90°$.

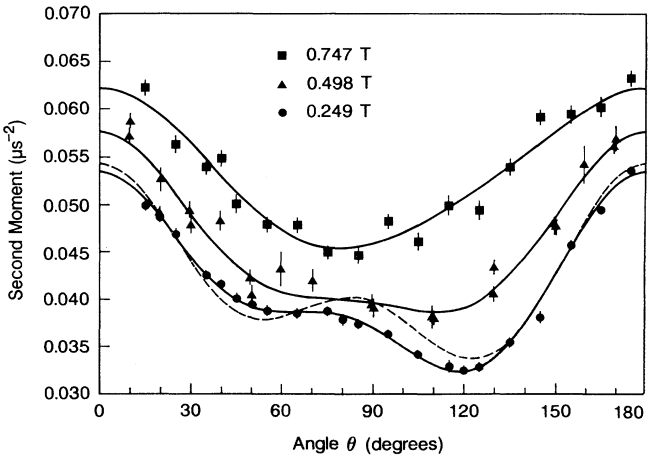

FIG. 2. Orientational dependence of the measured second moment in Bi at 11 K for three magnetic-field values and an azimuthal angle of $\phi = 90°$. The solid lines are fits of Eq. (2) to the data; the dashed line represents a fit to the data (not displayed) for 0.374 T. θ is defined as in Fig. 1.

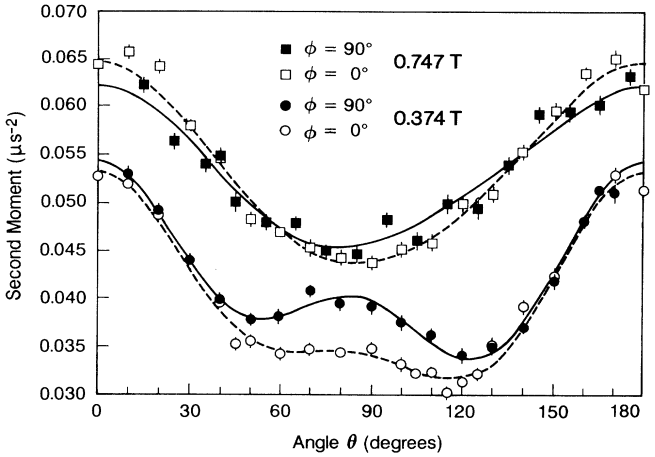

FIG. 3. Dependence of the experimental $M_2(\theta)$ on the azimuthal angle ϕ for two different field values. The solid lines are fits of Eq. (2) to the data keeping ϕ fixed at 90°. θ is defined as before.

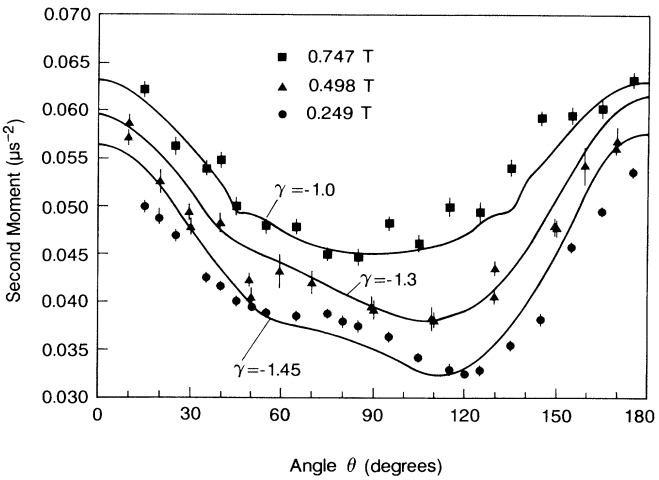

FIG. 4. Comparison of the $M_2(\theta)$ data (like in Fig. 2) with curves calculated according to the model of a rotated EFG (see text) for three field values assuming the same μ^+ site as in Fig. 1. In each case the isotropic part of the calculated distribution is normalized to the measured isotropic value.

not suited to describe the data.

The outlined theory leading to Eqs. (2), (3), and (5) does not leave much space for principle modifications. The calculation of the field distribution width at a given type of site arising from nuclear dipole moments at the host lattice sites is straightforward, involving no approximations. What one needs to know are the expectation values $\langle I_z \rangle$ and $\langle I_x \rangle$ at each nuclear site. These values are obtained from a diagonalization of the nuclear hyperfine Hamiltonian, which in our case includes only the Zeeman and the quadrupolar interaction. [An in principle possible contribution from a magnetic hyperfine interaction is dismissed as very unlikely in the semimetal Bi, so Eq. (4) represents the full nuclear hyperfine Hamiltonian.] The quadrupolar interaction involves, besides the well-known Bi quadrupolar moment, only the EFG tensor which in the above calculations was assumed to be of axial symmetry ($\eta_i = 0$) with the symmetry axis fixed along the axis connecting the μ^+ and a neighboring Bi nucleus. The actual form of the EFG tensor, however, is not of relevance with respect to the qualitative features of M_2 as pointed out before. Nevertheless, if we want to achieve agreement between the data and the calculations, the EFG is the only free parameter at our disposal. To make the EFG a truly free parameter it is necessary to drop the generally made assumption that the EFG at each nucleus possesses a fixed direction; i.e., we allow this direction to become an adjustable parameter, which implies that it may become a function of $\mathbf{B}_{\text{ext}}$.

This leads us to consider the following purely phenomenological model: For all magnetic-field values the nuclear spins are quantized along the *direction* of the EFG—this corresponds to a dominant quadrupolar interaction; the direction of the EFG, however, is assumed to be dependent on the strength and direction of the external field. A dominant quadrupolar interaction is suggested by the high-field results in that they approach an angular dependence given by Eq. (5). Further, we assume that the angle between $\mathbf{B}_{\text{ext}}$ and the EFG at a given nucleus for a given orientation of the crystal is given by $\gamma\alpha$, where α is the angle between $\mathbf{B}_{\text{ext}}$ and the EFG in zero applied field and γ is an *ad hoc* parameter representing a rotation of the EFG either toward $\mathbf{B}_{\text{ext}}$ if positive or away from $\mathbf{B}_{\text{ext}}$ if negative. $\gamma = 0$ or $\gamma = 1$ corresponds to the high-field Zeeman limit or the quadrupolar interaction limit, respectively. If $|\gamma\alpha|$ at a given nucleus exceeds 180°, it is fixed at this value. γ is assumed not to depend on the direction of $\mathbf{B}_{\text{ext}}$. Using this model $M_2(\theta,\phi)$ was calculated for various γ. Figure 4 shows that the curves obtained for $\gamma = -1.0$, -1.3, and -1.45 reproduce qualitatively the data in 0.747, 0.498, and 0.249 T, respectively. The 0.374-T data are well reproduced when $\gamma = -1.42$ is chosen (not shown in Fig. 4). Also, the minimal ϕ dependence of the data is well accounted for by this model. Quantitatively the agreement between the data and the calculations is, of course, not perfect. This is not surprising in view of the crudeness of the model. Therefore, both the sign and the field dependence of γ may not have a very deep meaning. The point, however, which we want to emphasize is the unavoidable conclusion that the EFG must be strongly coupled to $\mathbf{B}_{\text{ext}}$, even at very small values of B_{ext}.

Since the EFG is determined by the charge distribution in the vicinity of the Bi nuclei, it is in fact the charge distribution which must depend on B_{ext}. We do not know of any earlier work in which such a phenomenon was observed or anticipated. It is not clear to us what kind of physics underlies the observed phenomenon. It is possible

that strong spin-orbit coupling effects are involved which are known to be very important in Bi. One may also have to take into consideration that the present results are induced by the presence of the μ^+.

In summary, we have found that the field-dependent angular dependence of the second moment of the nuclear dipolar field distribution sensed by positive muons implanted in a Bi single crystal below 12 K cannot be explained within the framework of a well-established theory (the Van Vleck theory and its extension) unless one allows the direction of the electric-field gradient to depend on the direction and magnitude of the external field, even at very small fields. This would imply that the charge distribution around the Bi atoms in the neighborhood of the muon depends on the external magnetic field, a conclusion which we cannot justify by other arguments. It should be noted, however, that the anomalous angular dependence of the muon Knight shift in Bi in the same temperature regime is equally little understood [6,11] and might be explained in the same way.

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