Higher-Order Angular Dependence of the Positive-Muon Knight Shift in Bismuth

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The μ^+ Knight shift in rhombohedral Bi below 10 K is found to exhibit an anisotropy of solely fourth order in the direction cosines, or explicitly a $\sin^2(2\theta)$ dependence, where θ is the angle between the c axis and the applied magnetic field. The implications of this dependence, allowed by symmetry arguments but never seen before in NMR studies, are discussed. In addition, the lattice site of the μ^+ below 10 K has been determined and a local lattice contraction of approximately 11% was observed.

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The most general expression for the anisotropic Knight-shift constant in terms of the direction cosines λ_i of the applied field B, consistent with time-reversal invariance, is of the form (Rubens *et al.*[1])

$$K_{\rm an}(\boldsymbol{\lambda}) = K_{\rm iso} + \sum_{\alpha,\beta} B_{\alpha\beta}\lambda_\alpha\lambda_\beta + \sum_{\substack{\alpha,\beta\\ \gamma,\delta}} C_{\alpha\beta\gamma\delta}\lambda_\alpha\lambda_\beta\lambda_\gamma\lambda_\delta + \ldots . \quad (1)$$

$K_{\rm iso}$ is the isotropic Knight-shift constant and $B_{\alpha\beta}$ and $C_{\alpha\beta\gamma\delta}$ are second, fourth, etc., (even) rank tensors, respectively. The λ_i's are defined with respect to a coordinate system fixed with respect to the crystalline axes. Since $K_{\rm an}(\boldsymbol{\lambda})$ has to be invariant under the symmetry operations belonging to the point group appropriate for the considered crystalline site, many of the tensor components will vanish. In systems with cubic symmetry Eq. (1) reduces to (with neglect from now on of contributions beyond fourth order)

$$K_{\rm an}(\boldsymbol{\lambda})_{\rm cubic} = K_{\rm iso} + C(\lambda_x^4 + \lambda_y^4 + \lambda_z^4 - \tfrac{3}{5}), \quad (2)$$

while in uniaxial systems with C_{3v} or D_{3d} point symmetry one obtains

$$K_{\rm an}(\lambda)_{C_{3v},D_{3d}} = K_{\rm iso} + K_{20}P_2^0(\cos\theta) + K_{40}P_4^0(\cos\theta) + K_{43}P_4^3(\cos\theta)\cos(3\phi). \quad (3)$$

P_l^m here and in all other equations are normalized associated Legendre polynomials. θ is the angle between magnetic field and the threefold (or maximum) symmetry axis and ϕ is the azimuthal angle. The coefficients can be calculated from the magnetic hyperfine coupling of electronic and nuclear spins and not all coefficients allowed by symmetry may actually occur.

For example, if the electrons, polarized by the external field B, couple to the nuclear spin by the dipole-dipole interaction only, Eq. (1) assumes the simplified form[2]

$$K_{\rm an}(\lambda) = AP_2^0(\cos\theta) + (B_1\sin\phi + C_1\cos\phi)P_2^1(\cos\theta) + (B_2\sin 2\phi + C_2\cos 2\phi)P_2^2(\cos\theta). \quad (4)$$

In cubic systems $A = B_1 = B_2 = C_1 = C_2 = 0$ while in hexagonal and trigonal systems $A \neq 0$ and $B_1 = B_2 = C_1 = C_2 = 0$.[2] In any case, quite independently of the crystal symmetry, the general angular dependence of $K_{\rm an}$ does not involve fourth- and higher- order contributions in the direction cosines.

However, fourth- order contributions in the direction cosines will appear if the electron g factor, so far assumed to be isotropic in the derivation of Eq. (4), has to be replaced by an anisotropic tensor as a result of spin-orbit coupling. This was first shown by Boon[2] who considered the effects of an anisotropic g factor on the Knight shift originating from dipolar fields.

An anisotropic g factor will also lead to an anisotropy in that part of the Knight shift which originates from the isotropic Fermi contact hyperfine interaction, as first pointed out by Weinert and Schumacher[3] and Rubens *et al.*[1] This anisotropy includes terms of fourth order in the direction cosines as well.

Nuclear Knight-shift studies in noncubic systems have in many instances[4] revealed anisotropies well described by Eq. (4). Consistent with Eq. (4) no anisotropies were observed in cubic systems. As discussed above the presence of spin-orbit effects should produce anisotropies of fourth order in the direction

cosines also in cubic metals [Eq. (2)]. A search for such an effect in Pb by Schratter and Williams[5] yielded indeed a small anisotropy of the correct angular dependence. Unfortunately this result could not be confirmed in a more detailed investigation in Pb and Pt by Rubens *et al.*[1] We are thus left with the situation that all experimental results on the anisotropy of the nuclear Knight shift are consistent with Eq. (4) and angular dependences of the form of Eq. (2) or (3) have possibly been seen only in one instance.[5]

In this contribution we report on the first clear observation of an anisotropic Knight shift of fourth order in the direction cosines in the rhombohedral semimetallic system bismuth. The "nuclear" spin probe used in this system was the positive muon implanted interstitially in the sample.

The crystal structure of Bi (space group D_{3d}^5-$R_{3\bar{m}}$) can be viewed as a simple cubic lattice distorted along the body diagonal to yield a rhombohedral structure. In addition the atoms' positions are shifted such as to produce hexagonal layers of alternating distances (see Fig. 1). While in the ideal rhombohedral structure only one type of interstitial site is available (as in the simple cubic structure), the staggered sequence of layers leads to the appearance of two types of interstitial sites, both of which are associated with the crystallographic point group D_{3d}. The most general expression for the anisotropic muon Knight shift is therefore given by Eq. (3).

The experiments were performed at the Swiss Institute for Nuclear Research (SIN) by use of the high-precision stroboscopic muon spin-rotation spectrometer.[6,7] The spin-polarized positive muons (μ^+) were stopped in a high-purity (99.999%) single crystal of spherical shape. The crystal axes were determined by x ray and neutron diffraction. The μ^+ Larmor precession was observed in a field of roughly 0.746 T. The angular dependence of the Knight shift was measured by rotation of the crystal around one of the three twofold axes perpendicular to the threefold c axis. Thus only the angle θ between field and the c axis was varied while the azimuthal angle ϕ was kept at 90°.

The observed Knight shift at 3.8, 8, and 20 K is shown in Fig. 2. As can be seen the Knight shift is generally negative. At 20 K the angular dependence obtained is

$$K^{20\,\mathrm{K}}(\lambda) = -309.0 - 18.8 P_2^0(\cos\theta)\ \text{ppm}, \qquad (5)$$

consistent with Eq. (4) and the point group D_{3d}. (At higher temperatures it is found that the anisotropic term changes its sign, but the general angular dependence is unchanged. This will be discussed elsewhere.) The 20-K result is thus well in line with other NMR determinations of $K_{\mathrm{an}}(\lambda)$ in noncubic systems. At 8 and 3.8 K, however, we find a drastic change of $K_{\mathrm{an}}(\lambda)$ which is now very well represented by the expression

$$\begin{aligned} K_{\mathrm{an}}(\lambda) &= -296.9 - 16.9 P_2^0(\cos\theta) \\ &\quad + 39.8 P_4^0(\cos\theta)\ \text{ppm} \\ &= -[273.5 + 43.5\sin^2(2\theta)]\ \text{ppm}. \end{aligned} \qquad (6)$$

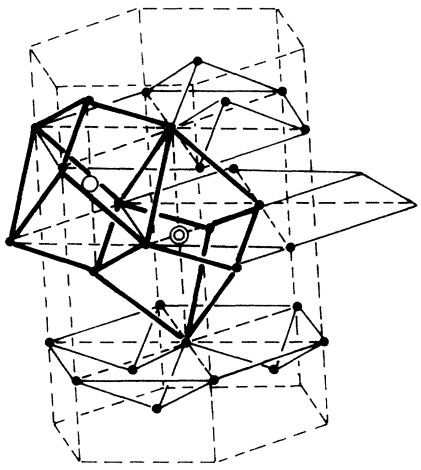

FIG. 1. Schematic view of the rhombohedral lattice structure of Bi. Indicated are the two possible μ^+ sites which are located either between two more widely spaced (circle: No. 1) or between two more closely spaced (double circle: No. 2) hexagonal planes.

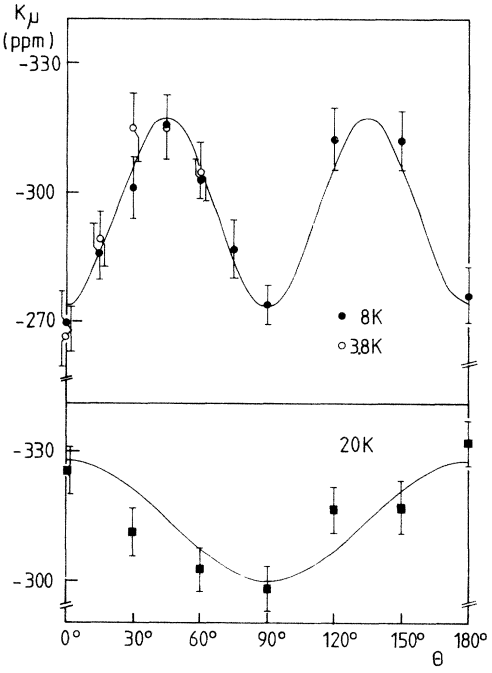

FIG. 2. Angular dependence of the μ^+ Knight shift below 10 K and at 20 K. θ is the angle between magnetic field and c axis.

This expression is consistent with Eq. (3) (note that $\cos 3\phi = 0$) but it implies a contribution of *fourth order* in the direction cosines, of totally unexpected magnitude.[8]

Before we discuss this latter result further it is important to know the μ^+ site in Bi and perhaps the response of the lattice environment to the presence of the μ^+. This information can be obtained from a detailed study of the anisotropy of the second moment M_2 of the dipolar field distribution at the μ^+. The origin of the dipolar fields is the Bi nuclei. The general angular dependence of M_2 can be found by symmetry considerations in the same way as for the Knight shift.[9] The experimental results on M_2 in Bi at 3.8 and 8 K are displayed in Fig. 3 for both zero field and a field of 0.746 T. The zero-field data were obtained by the time-differential muon spin-rotation technique;[7]

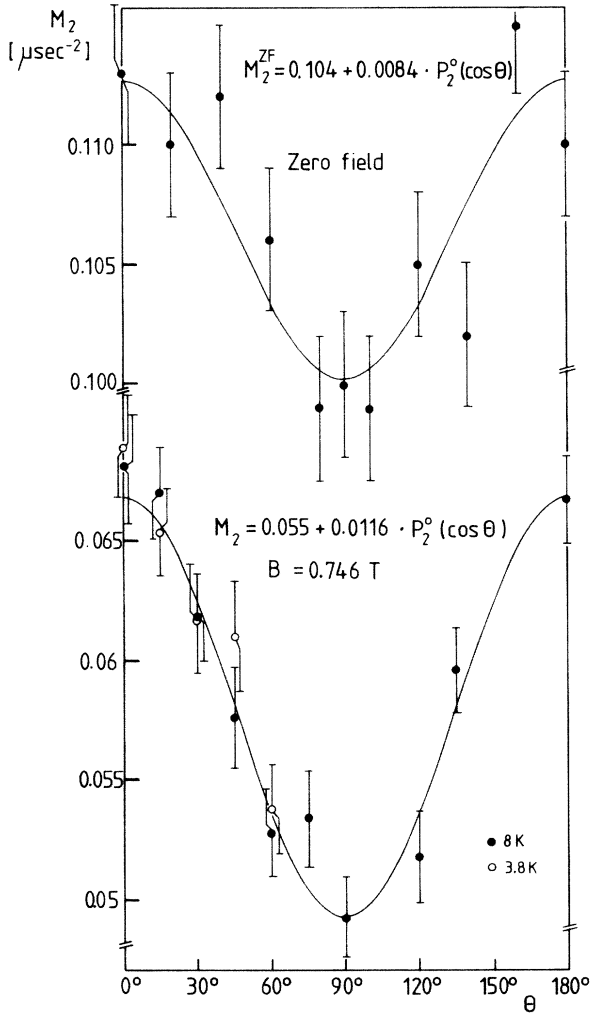

FIG. 3. Angular dependence of the second moment of the dipolar field spread from the Bi nuclei at the μ^+ obtained in zero and in transversely applied field below 10 K. θ is the angle between magnetic field and c axis.

the 0.746-T data are a byproduct of the Knight-shift measurements. It should be noted that the observed anisotropy of M_2 in zero field is the first such observation. It can only be observed in noncubic systems. In both cases we find an angular dependence of the form

$$M_2 = M_2^{\text{iso}} + M_{20} P_2^0(\cos\theta), \tag{7}$$

which contrasts clearly with the angular dependence of the Knight shift and underlines its unusual behavior. Analysis of these data, the details of which will be discussed elsewhere, places the μ^+ at site No. 1 in Fig. 1. The $P_2(\cos\theta)$ distribution implies in particular that the six nearest Bi neighbors (nn) are subject to a very strong quadrupole interaction (dominating also at 0.746 T) involving electric field gradients directed radially away from the μ^+. Next-nearest, etc., neighbors, on the other hand, are subject to electric field gradients along the c axis, as is known from other studies.[10] It is interesting to note that a μ^+ assignment to site No. 2 in Fig. 1 leads to a reversed anisotropy in clear contradiction with the data. Another, and most remarkable, result of the analysis is the observation of a lattice *contraction* around the μ^+; i.e., the six nearest neighbors and the two next-nearest neighbors (nnn) are shifted by 11% closer to the μ^+. This constitutes the first observation of a lattice contraction around a hydrogenlike impurity in a metal. This contraction may also explain qualitatively the appearance of extremely strong radial electric field gradients at the nn Bi nuclei. Only the simultaneous analysis of both the zero- and transverse-field data allowed the identification of the nn and nnn Bi positions.

At 20 K the second moment appears to be much reduced with no significant anisotropy within the statistical accuracy. Since the relaxation rate is independent of temperature from 20 K up to 60 K in agreement with Barsov *et al.*,[11] this reduction does not seem to arise from a motional narrowing effect due to long-range μ^+ diffusion. Hence we conjecture that for temperatures $20\ \text{K} \leq T \leq 60\ \text{K}$ another site occupation is observed. Whether this might also provide an explanation of the type of Knight-shift anisotropy at 20 K will be the subject of further studies.

The peculiar Knight-shift anisotropy below 10 K is thus associated with a μ^+ occupation of site No. 1 together with a sizably contracted nearest-neighbor environment. The "pure" $\sin^2(2\theta)$ dependence indicates that mainly fourth-order terms in the direction cosines are present while contributions in second order in the direction cosines appear to be largely suppressed.

This latter feature may be taken as an indication that the anisotropy is not associated with the contact hyperfine field but with the dipole-dipole interaction arising from more distant electrons modified by spin-orbit interaction. If the first possibility were true one would

have expected primarily an anisotropy of second order in the direction cosines.[1,3] On the other hand, if the effect of the orbital motion of the electrons on the spin alignment through the anisotropic g factor and its effect on the dipole-dipole coupling is considered, fourth-order effects arise naturally since the anisotropic g factor and the dipole-dipole interaction each lead to effects which are of second order in the direction cosines.

In the treatment of Boon[3] and Rubens *et al.*[1] the electronic dipolar fields at the nuclear probe are considered to be of spin origin only and furthermore spin-orbit coupling is assumed to produce only a small perturbation in the free-electron g factor. However, susceptibility[12] and g-tensor[13] studies in Bi have revealed pronounced anisotropy effects and electron g factors far away from the free value. From these results it is obvious that orbital effects must play an important role.[14] In particular, the strongly diamagnetic susceptibility of Bi seems to point to sizable orbital contributions associated with electrons in the fully occupied valence bands.[14] It is thus quite likely that electronic dipolar fields at the interstitial μ^+ are not only of spin but also of orbital origin, induced by the applied field (induced diamagnetism). Again one predicts terms of fourth and second order in the direction cosines in the Knight shift.

The absence of second-order terms in Eq. (6) may be traced back to the properties of the effective g tensor or the induced magnetic moments of the electrons, including orbital contributions. If these moments were to vary like $3\sin^2\theta - 1$ the resulting dipolar Knight shift would show the same angular dependence as Eq. (6): $K_{\rm dip} \propto (3\cos^2\theta - 1)(3\sin^2\theta - 1) = [\frac{9}{4}\sin^2(2\theta) - 2]$.

As Eq. (6) shows, the μ^+ Knight shift is dominated by a large and *negative* isotropic contribution. Although this looks like a contact hyperfine field effect, the negative sign excludes an explanation on the basis of some Pauli-type spin paramagnetism.[15] In this context one has to remember that Bi is a semimetal with only $\sim 3\times 10^{17}$ conduction electrons/cm^3.[13] This is more than five orders of magnitude less than in Cu. It is not known how the screening of the positive muon charge under such circumstances has to be described. Perhaps the strong lattice contraction around the μ^+ is an indication for the formation of a μ^+-Bi chemical complex and the negative sign of the isotropic Knight shift would have to be explained on the basis of the electronic structure of this complex invoking again orbital effects. It is interesting to mention that the μ^+ Knight shift in Sb, another semimetal, has been determined to be positive and anomalously large ($\sim 1\%$).[16]

In summary we have observed for the first time an anisotropic Knight shift of solely *fourth order* in the direction cosines by studying the Knight shift of positive muons implanted in monocrystalline Bi below 10 K. We believe this to be the result of an anisotropic electron g factor and/or induced anisotropic effective magnetic moments (including orbital terms) and nonzero electronic dipole fields at the μ^+ site. The position of the μ^+ was determined and it was found that the nearest and next-nearest neighbors were shifted towards the μ^+ by as much as 11%.

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