[2]C. B. Duke and G. E. Laramore (unpublished).
[3]P. J. Feibelman, Phys. Rev. 176, 551 (1968), referred to as I in the text.
[4]E. A. Stern and R. A. Ferrell, Phys. Rev. 120, 130 (1960).

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Comments on the Knight Shift in Bismuth and Other p-Band Diamagnetic Metals

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The role of p-polarization and conduction-electron diamagnetism in some diamagnetic metals and intermetallic compounds, which have negative Knight shifts, is examined.

It has been known for some time that the diamagnetic susceptibility contributes a negative term, κ_{dia}, to the Knight shift $\mathcal{K}$. The first expression was given by Das and Sondheimer[1] and applied particularly to Be. They obtained, in the free-electron approximation,

$$\mathcal{K}_{dia}=\frac{8\pi}{3}\chi_{dia} \tag{1a}$$

$$=-\frac{8\pi}{3}\left(\tfrac{1}{3}\chi_p\right)\left\langle\frac{m}{m^*}\right\rangle^2, \tag{1b}$$

where the symbols have their usual meanings. The Pauli and diamagnetic conduction-band susceptibilities χ_p and χ_{dia} are in volume units. One purpose of this paper is to point out that the above term may be significant in diamagnetic metals and semimetals other than Be, such as Bi, Te, NaTl, and BiIn, which have a negative $\mathcal{K}$ (p-electron atom sites sampled by $\mathcal{K}$ are underlined). Now, there exist mechanisms other than $\mathcal{K}_{dia}$, which may make negative contributions to $\mathcal{K}$. One of these is p-electron core polarization, and it has recently been fashionable to attribute the above and certain other negative Knight shifts to this term. The purpose of the present comment is to indicate that there are quantitative difficulties with this attribution. It appears likely that $\mathcal{K}_{dia}$ predominates at least in Bi and Be, and that this and other mechanisms are important to certain compounds. It will also become clear that the understanding of p-core polarization effects is grossly inadequate, the situation being far worse than that for d-core polarization effects in transition metals.

Subsequent to the work of Das and Sonheimer, Das and co-workers made energy band estimates[2] of a number of the Knight-shift contributions in Be. These calculations emphasized the contribution of p-core polarization to the negative Knight shift. Recently it has been concluded[3] that the p term, as deduced from the calculations, cannot be responsible for the observed negative $\mathcal{K}$ and that $\mathcal{K}_{dia}$ must predominate. Be is a somewhat special case in that its $\mathcal{K}$ is small (-0.0025%)[4] as well as negative. The other materials which we will consider have significantly larger negative $\mathcal{K}$ values. In the remainder of this comment we will inspect $\mathcal{K}_{dia}$, p-core polarization, and other negative terms. This will be followed by consideration of the experimental situation for Bi and some of the compounds.

It has been pointed out[5] that the Knight shift arising from the orbital electronic currents can be conveniently divided into two parts: One including Eq. (1) and a second one associated with the short-range part of the orbital hyperfine interaction. Using the tight-binding scheme, Clogston *et al.* obtained,[6] an alternative description of the short-range part which includes the Van Vleck or orbital Knight shift, and a term of the form

$$\mathcal{K}_2=\frac{8\pi}{3}\chi_{dia}\frac{\langle r^{-1}\rangle}{\langle r^2\rangle}r_{WS}^3, \tag{2}$$

where χ_{dia} is the single-site diamagnetism and r_{WS} the Wigner-Seitz radius. For the tight-binding wave functions involved, the $\langle r^{-1}\rangle r_{WS}^3/\langle r^2\rangle$ factor will generally have a value in excess of 10 thus enhancing the diamagnetic Knight shift. It is, of course, not clear that such a tight-binding description is relevant to a p-band metal. There are additional terms, in either the Clogston[6] or Hebborn[5] description, whose behaviors are not clearly discernible.[7] We will em-

ploy Eq. (1) alone when estimating $\mathcal{K}_{dia}$. This presumably underestimates the effect. Equation (1) yields rather different estimates of $\mathcal{K}_{dia}$ depending on whether one uses the first or second line. The first line requires an estimate of χ_{dia} which can be done by taking the total χ and subtracting out an estimated ion core diamagnetism. It neglects the presence of any Pauli term and hence provides a minimum estimate of χ_{dia} and $\mathcal{K}_{dia}$. Taking maximum experimental values for m/m^* (when available), and estimating χ_p (say from electronic specific-heat data), one can obtain $\mathcal{K}_{dia}$ from the second line of Eq. (1). This provides much larger estimated values for $\mathcal{K}_{dia}$. Both schemes will be used.

The above-mentioned orbital term is approximately written as

$$\mathcal{K}_{VV} = \frac{8\pi}{3} \chi_{VV} \langle r^{-3} \rangle r_{WS}^3, \tag{3}$$

where χ_{VV} is the orbital susceptibility in volume units. In this form, $\mathcal{K}_{VV}$ is positive. Treated in detail, the precursor to Eq. (3) could[8] be negative. This could arise from the behavior of the off-diagonal orbital hyperfine matrix element through bands where there was radically varying wave-function character above and below the Fermi level. We expect that under such circumstances the orbital term will be insignificantly small.

Experimental core-polarization hyperfine fields (per valence p electron) H_p of roughly -50, -150, and -300 kG/μ_B are observed for atomic As, Sb, and Bi, respectively.[9] These are S-state atoms in the ns^2np^3 configuration and hence the p shell cannot interact directly with the nucleus via spin-dipolar or orbital terms. It thus interacts indirectly via the spin polarization of the paired s shells.[10,11] H_p data do not exist for adjacent non-S-state atoms due to the competition of the orbital and spin-dipolar terms. As a result, the above listed H_p values are generally employed for any member of a particular p-shell row in the Period Table. H_p enters the p-band Pauli term in $\mathcal{K}$ via

$$\mathcal{K}(p) = (1/\mu_B) H_p \chi_p(p), \tag{4}$$

where $\chi_p(p)$ refers to the p-electron Pauli susceptibility. There are two shortcomings in using the fixed H_p values here. First, there is no reason to expect that H_p is a constant across such a row. Recent exchange polarized Hartree-Fock calculations[11] for the $2p$, $3p$, and $4p$ rows of atoms fail to reproduce the known As (N and P) value(s) but do suggest that H_p for Ga, In, and Tl may be as much as twice the respective As, Sb, and Bi values. Second (the more serious to the use of the H_p), is that they include the polarization response of the ns^2 *valence* s-shell electrons which go into the bottom of the conduction band in the metal. The calculations indicate that this term is important to the atomic H_p (and negative). The H_p, appropriate to Eq. (3), should include the polarization response of the paired valence s character throughout the occupied bands, as well as that of the ion core, but there arises the question of how this has been perturbed on going into the metal[12,13] Essentially nothing is known concerning this matter for the metals under consideration here.

There are other mechanisms that can produce negative hyperfine fields. For example, the core-polarization response to either d or f electrons also makes a negative contribution to $\mathcal{K}$ but does not concern us here. Also, there may be intersite contributions to $\mathcal{K}$, i.e., the hyperfine field due to spin moments induced on neighboring sites. The Al resonance in $GdAl_2$ is an example[14] of this: The Al Knight shift is completely dominated by the alignment of the Gd $4f$ shells in the external field. Significant intersite effects can arise in circumstances involving less extreme differences in atomic character (i.e., even in an elemental metal) and they make positive or negative contributions to $\mathcal{K}$.

There is also an orbital mechanism[15] that can produce negative Knight shifts. This term involves the possibility of a sign reversal in the electronic g factor (and hence spin direction) and has been employed for semiconductors. For example, this term has been used to explain $\mathcal{K}$'s of opposite sign in n- and p-type PbTe,[16] where the g factors have opposite signs. For the case of Bi, the g factor has the same sign as the electron[17] and therefore this mechanism does not apply. For the other compounds of interest to us here, the g factor is not known.

Bi has a substantial negative shift of -1.25%.[18] Since the metal is diamagnetic, we employ the electronic specific heat ($\gamma = 0.021 \times 10^{-3}$ J/mole K^{-2})[19] to obtain χ_p. The equation

$$H_{exp} \equiv \mu_B \mathcal{K}_{exp} / \chi_p \tag{5}$$

yields an experimental effective field of $-250\,000$ kG/μ_B which is almost three orders of magnitude larger than the experimental H_p (-300 kG/μ_B) for atomic Bi.[20] This discrepancy may be somewhat reduced by consideration of g factor and other effects, but it seems unrealistic to attribute the large negative H_{exp} value to p polarization.

In order to compare with diamagnetic shifts it is convenient to rewrite Eq. (1) in order to describe the diamagnetic term as an effective field, namely,

$$H_{dia} \equiv \mu_B (\mathcal{K}_{dia} / \chi_p), \tag{6a}$$

$$H_{dia} = 15.6 (\rho/A) \langle m/m^* \rangle^2 \times 10^3, \tag{6b}$$

where ρ and A are the density and atomic weight of the metal, respectively. Using an extreme experimental m^*/m value[21] of 0.002, Eq. (6b) yields an H_{dia} of $-160\,000$ kG/μ_B, while an estimate of χ_{dia}

from the experimental χ (see the earlier discussion of this) yields, from Eq. (6a), $H_{dia} = -3200$ kG/μ_B. We see that under the extreme circumstance encountered in Bi, of a small χ_p and significant diamagnetism, the diamagnetic effect can be equivalent to a huge hyperfine field. Incidentally, we note that although a calculation of $\mathcal{K}_{dia}$ using the first part of Eq. (1) leads to $\mathcal{K}_{dia} \sim -0.01\%$ [22] for Bi, the second part of Eq. (1) gives a $\mathcal{K}_{dia} \sim -1\%$ when a specific heat χ_p [23] and $m^*/m = 0.002$ [21] are used. When attempting to compare H_{dia} and H_p with H_{exp} it should be remembered that there will be at least some positive contribution to $\mathcal{K}$: There will be some s character in the Fermi-surface orbitals and thus an even larger H_{dia} or H_p is required to account for the negative shift. [24]

In view of the above it would appear that it is impossible for p polarization to be responsible for the Bi Knight shift and that the diamagnetic term is a more reasonable candidate. A better estimate than that obtainable with Eq. (1) is needed.

Tellurium is another example of a material with a negative Knight shift (−0.06% with respect to $TeCl_2$). [25] Te is diamagnetic, with $\chi_{exp} = -39.5 \times 10^{-6}$ emu/mole. [26] Here too, p polarization alone is not large enough to explain the Knight shift, but with m^* values as low [27] as $0.04m_0$, the diamagnetic term appears to be a possible source of the shift.

The analysis of compounds is complicated by the fact that the χ_p appropriate to Eqs. (4)–(6) is that fraction of the Pauli susceptibility appropriate to the atomic site in question. The analysis of the diamagnetic compounds NaTl and BiIn is further complicated by the lack of knowledge of χ_p (or γ). The Tl [28–30] and In [31] shifts are −0.92% and −0.18% at 77 K, respectively, in these two compounds. Crude estimates, using elemental metal specific-heat data [23] γ_{Tl} and γ_{In}, yield H_{exp} values for NaTl and BiTl which, at a minimum, are of the same order of (although larger than) the respective H_p (see the discussion above). It must be remembered that these compounds are likely to have much smaller paramagnetic susceptibilities (and electronic specific heats) than the elemental metals Tl and In and this could lead to an H_{exp}/H_p which might be several orders of magnitude larger than those estimated here. Estimates of $\mathcal{K}_{dia}$ for BiIn are two to eight percent of $\mathcal{K}_{exp}$, depending on how Eq. (1) is used, and are smaller for NaTl. That is, for these two compounds the diamagnetic term may approach the magnitude of the p-polarization effects.

There is an interesting correlation obtained on inspecting NaIn, LiIn, LiGa, and LiAl which are isostructural and isovalent with NaTl. These are essentially nonmagnetic, [32,33] i.e., their susceptibilities, after the subtraction of core diamagnetism, are essentially zero and they have essentially vanishing Knight shifts. The shifts are, respectively, 0.07, [34] 0.13, 0.09, and 0.01%. [30] These contrast with NaTl which is the most diamagnetic by a significant margin [33] and has a strong diamagnetic shift as noted above. In other words the above Knight-shift data display no trend reflecting the variation in H_p from Al to Ga to In. It thus appears that the p-polarization term is small in NaIn, LiIn, LiGa, and LiAl, while in order to explain the NaTl Knight shift by p polarization, an H_p would be required which is enhanced by almost an order of magnitude over its atomic value. We conclude that if an explanation for the NaTl Knight shift is sought in terms of p polarization, quantitative justification is still lacking.

There are other compounds where p polarization is usually invoked and where it is in some numerical difficulty. For example, Ga site H_{exp} values of −300 and −400 kG/μ_B have been deduced from the measured [35–37] Knight shifts in V_3Ga and $AuGa_2$, respectively. These values probably underestimate [37] the actual magnitudes of the H_{exp}. They are to be compared with the As H_p of −50 kG/μ_B. Again p polarization, as defined by the experimental H_p values, appears in difficulty. We do not believe $\mathcal{K}_{dia}$ is responsible here although the observed [38] m^*/m (of 0.175) for $AuGa_2$ yields an H_{dia} of −60 kG/μ_B. We believe instead that intersite effects dominate. These intersite effects arise from the spin polarization induced at neighboring V or Au sites via the Pauli term, much as it does in more obvious cases, such as $GdAl_2$.

In conclusion, p polarization, as calibrated by experimental S-state atom H_p values, appears in difficulty for a variety of cases for which it has been invoked. Close inspection suggests that diamagnetism is not negligible to the Knight shifts in Bi as well as Be and perhaps some of the diamagnetic p-band compounds. A more complete treatment of the diamagnetic terms is needed as are theoretical and experimental investigations into the effect of p polarization on paired states in occupied conduction bands.

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[1] T. P. Das and E. H. Sondheimer, Phil. Mag. 5, 529 (1960).

[2] Wei Mei Shyu, G. D. Gaspari, and T. P. Das, Phys. Rev. 141, 603 (1966); P. Jena, S. D. Mahanti, and T. P. Das, Phys. Rev. Letters 20, 544 (1968).

[3] P. Jena, T. P. Das, and S. D. Mahanti, Phys. Rev. B 1, 432 (1970). J. Gerstner and P. H. Cutler, Phys. Letters 30A, 368 (1969); in *Proceedings of the Symposium*

on Electronic Density of States, Gaithersburg, Md., 1969, Natl. Bur. Std. Special Publication No. 323 (U. S. GPO, Washington, D. C., 1970).

[4]W. T. Anderson, Jr., M. Ruhlig, and R. R. Hewitt, Phys. Rev. 161, 293 (1967); D. E. Barnaal, R. G. Barnes, and B. R. McCart *ibid.* 157, 510 (1967).

[5]Y. Yafet, J. Phys. Chem. Solids 21, 99 (1961); J. E. Hebborn, Proc. Phys. Soc. (London) 80, 1237 (1962); M. J. Stephen, Phys. Rev. 123, 126 (1961); J. E. Hebborn and M. J. Stephen, Proc. Phys. Soc. (London) 80, 991 (1962).

[6]A. M. Clogston, V. Jaccarino, and Y. Yafet, Phys. Rev. 134, A650 (1944).

[7]T. B. Smith, J. Phys. C 3, 1159 (1970).

[8]T. P. Das (private communication).

[9]G. H. Fuller and V. W. Cohen, *Nuclear Data Tables* (Academic, New York, 1969), Vol. 5, p. 433.

[10]See, e.g., R. E. Watson and A. J. Freeman, in *Hyperfine Interactions*, edited by A. J. Freeman and R. B. Frankel (Academic, New York, 1967).

[11]P. S. Bagus, B. Liu, and H. F. Schaefer, III, Phys. Rev. A 2, 555 (1970).

[12]R. E. Watson and A. J. Freeman, Phys. Rev. 123, 2027 (1961); R. A. Moore and S. H. Vosko, Can. J. Phys. 46, 1425 (1968); 47, 1331 (1969).

[13]S. D. Mahanti, L. Tterlikkis, and T. P. Das in *Magnetic Resonance*, edited by C. K. Coogan, N. S. Ham, S. N. Stuart, J. R. Pilbrow, and G. V. H. Wilson (Plenum, New York, 1970), p. 91; P. Jena, T. P. Das, and S. D. Mahanti, Phys. Rev. B 1, 432 (1970).

[14]V. Jaccarino, J. Appl. Phys. 32S, 102 (1961); E. D. Jones and J. I. Budnick, J. Appl. Phys. 37, 1250 (1966).

[15]See, e.g., Y. Yafet, J. Phys. Chem. Solids 21, 99 (1961).

[16]S. D. Senturia, A. C. Smith, C. R. Hewes, J. A. Hofmann, and P. L. Sagalyn, Phys. Rev. B 1, 4045 (1970).

[17]G. E. Everett, Phys. Rev. 128, 2564 (1962); G. E. Smith, J. K. Galt, and F. R. Merritt, Phys. Rev. Letters 4, 276 (1960).

[18]B. F. Williams and R. R. Hewitt, Phys. Rev. 146, 286 (1966).

[19]N. E. Phillips, Phys. Rev. 118, 644 (1965).

[20]R. L. Christensen, D. R. Hamilton, H. G. Bennewitz, J. B. Reynolds, and H. H. Stroke, Phys. Rev. 122, 1302 (1961).

[21]A. H. Kahn and H. P. R. Frederikse, in *Solid State Physics* edited by F. Seitz and D. Turnbull (Academic, New York, 1959), Vol. 9, p. 281.

[22]$\chi_{cond}^{dia} \equiv \chi_{exp}^{dia} - \chi_{core}^{dia} = -230\times10^{-6}$ emu/mole was used, with χ_{exp}^{dia} taken from Ref. 26 and χ_{core}^{dia} taken from C. M. Hurd and P. Gooding, J. Phys. Chem. Solids 28, 523 (1967).

[23]R. R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, *Selected Values of Thermodynamic Properties of Metals and Alloys*, (Wiley, New York, 1963); and (unpublished).

[24]The minor component of the relativistic $p_{1/2}$ electron character also has a contact term (which is present in H_p as well as H_{exp}).

[25]M. Bensoussan, J. Phys. Chem. Solids 28, 1533 (1967).

[26]*Landolt-Börnstein Tables*, edited by K. H. Hellwege (Springer, Berlin, 1961), Vol. II, part 9.

[27]R. Beserman, thesis, U. Paris, 1962 (unpublished); as referenced in *Tables de Constantes, Constantes Selectionneés Relatives aux Semi-Conducteurs* (Pergamon, New York, 1961); C. Rigaux and G. Drilhon, J. Phys. Soc. Japan Suppl. 21, 193 (1966).

[28]N. Bloembergen and T. J. Rowland, Acta Met. 1, 731 (1953).

[29]L. H. Bennett, Acta Met. 14, 997 (1969).

[30]H. E. Schone and W. D. Knight, Acta Met. 11, 179 (1963).

[31]D. L. Radhakrishna Setty and B. D. Mungurwadi, Phys. Rev. 183, 387 (1969).

[32]Y. L. Yao, Trans. AIME 230, 1725 (1964).

[33]W. Klemm and H. Fricke, Z. Anorg. Allgem. Chem. 282, 162 (1955).

[34]L. H. Bennett, Bull. Am. Phys. Soc. 11, 172 (1966); and (unpublished).

[35]A. M. Clogston and V. Jaccarino, Phys. Rev. 121, 1357 (1961).

[36]V. Jaccarino, M. Weger, J. H. Wernick, and A. Menth, Phys. Rev. Letters 21, 1811 (1968).

[37]In the case of V_3Ga we employ Mattheiss's band calculations [L. F. Mattheiss, Phys. Rev. 138, A112 (1965)] to ascertain the weight of Ga vs V orbital character at the Fermi level, hence that fraction of χ_p associated with a Ga site, i.e., $\frac{1}{2}$ to $\frac{1}{3}$ per molecule. His results suggest that H_{exp} lies between -300 and -400 kG/μ_B. In the case of $AuGa_2$ it is necessary to employ the low-temperature $\mathcal{K}$ data and avoid the question of band repopulation effects (Ref. 36). The quoted H_{exp} assumes the wave-function character, hence χ_p, is entirely associated with Ga sites, and χ_p is derived from $\gamma = 2.70\times10^{-3}$ J mole$^{-1}K^{-2}$ [J. A. Rayne, Phys. Letters 7, 114 (1963)]. A value of -750 kG/μ_B is obtained if conduction electron diamagnetism is neglected and $\chi_p \equiv \chi_{exp} - \chi_{core}^{dia}$ is employed [χ_{core}^{dia} values were taken from C. M. Hurd and P. Coodin, J. Phys. Chem. Solids 28, 523 (1967)]. These all assume a susceptibility which is associated entirely with the Ga site, which is clearly not true {the Au site has substantial $\mathcal{K}$ [A. C. Switendick and A. Narath, Phys. Rev. Letters 22, 1423 (1969)}] and H_{exp} probably exceeds -500 or -800 kG/μ_B for V_3Ga and $AuGa_2$, respectively.

[38]J. P. Jan, W. B. Pearson, Y. Saito, N. Springford, and I. M. Templeton, Phil. Mag. 12, 1271 (1965).