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Temperature Dependence of the ^{115}In Nuclear-Magnetic-Resonance Spectrum in the Intermetallic Compound InBi

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The NMR spectrum of ^{115}In in the intermetallic compound InBi was recorded in the temperature range 77–390°K. The Knight shift and the quadrupole coupling constant at the site of the ^{115}In nucleus at each temperature have been determined. The Knight shift is positive at higher temperatures, decreases with decreasing temperature, and changes sign at about 230°K, whereas the quadrupole coupling constant, which is also a function of temperature, passes through zero at about 170°K. The results have been discussed in the light of the crystal structure of the compound. It has been shown that core polarization is responsible for the observed negative Knight shift at low temperatures.

INTRODUCTION

As reported earlier,[1] the nuclear magnetic resonance (NMR) spectrum of ^{115}In was recorded at room temperature in an InBi intermetallic compound. From the observed spectrum the isotropic Knight shift ($K_{\text{iso}}=+0.18\%$), the axial component of the Knight shift ($K_{\text{ax}}=0.02\%$) and the lowest pure quadrupole frequency ($\nu_Q=275$ kc/sec) at the site of the ^{115}In nucleus have been measured. Further, it has been observed[2,3] that the Knight shift in the compound changes appreciably on melting, whereas there is little change in the shift on melting in the pure metal.[4] This interesting observation has prompted us to conduct a detailed NMR study of the compound at various temperatures in the range 77–390°K.

EXPERIMENT AND RESULTS

The NMR measurements were made on a Varian Associates wide-line NMR spectrometer with its temperature accessory. The resonance spectrum of ^{115}In in the InBi intermetallic compound was recorded at various frequencies from 4 to 11 Mc/sec. Figure 1 shows the Knight shift (K) measured from the unperturbed position of the central line at 8 Mc/sec with reference to the ^{115}In resonance in an aqueous solution of In(NO$_3$)$_2$ and ν_Q determined from all four pairs of satellites as a function of temperature. (At high temperatures, where the signal-to-noise ratio was poor, ν_Q has been determined from the width of the central line broadened by the second-order quadrupole interaction.) The point corresponding to $\nu_Q=0$, observed at about 170°K, was obtained from the central-line-intensity consideration. An attempt has been made to determine K_{ax} of ^{115}In in the compound by the method outlined by Jones *et al.*[5] At room temperature K_{ax} is $+0.02\%$; at higher temperatures, as the signal-to-noise ratio (for the dc magnetic field available here) of the NMR spectrum was poor, a detailed evaluation of K_{ax} could not be made. A qualitative analysis of the line shapes, however, shows that K_{ax} increases with increasing temperature. At temperatures below 250°K the central line is almost symmetrical in shape, indicating the vanishing axial component of the Knight shift.

The bulk magnetic susceptibility (χ) of the compound has been measured at various temperatures in the range 77–400°K. It has been found that the sample is diamagnetic in the solid state and that χ decreases smoothly with increasing temperature (~-174 emu/mole at 77°K and ~-40 emu/mole at 350°K). In the molten state at 390°K the sample is feebly paramagnetic ($\sim+25.7$ emu/mole). The Knight shift versus susceptibility with temperature as an implicit parameter is plotted in Fig. 2.

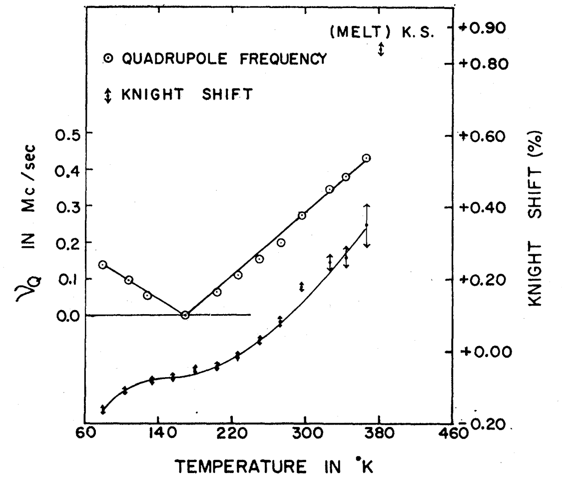

FIG. 1. Knight shift and lowest pure quadrupole frequency at the site of ^{115}In as a function of temperature in the intermetallic compound InBi.

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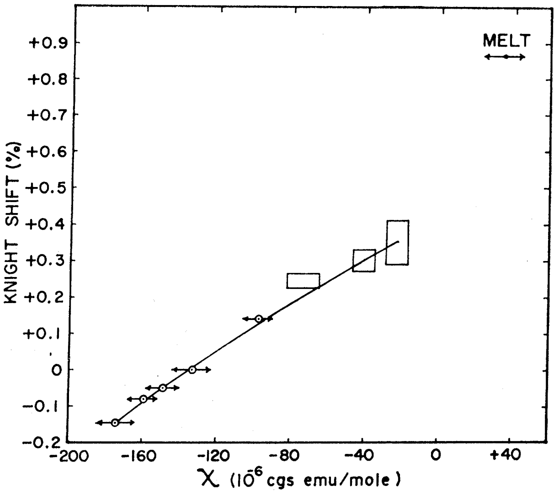

FIG. 2. Knight shift of ^{115}In versus bulk magnetic susceptibility with temperature as an implicit parameter in the intermetallic compound InBi.

InBi has a tetragonal structure of the PbO type,[6] the space group being *p*4/*nmm*. The lattice spacings of the compound were determined at four temperatures from the x-ray powder patterns and the measured lattice parameters are given in columns 2 and 3 of Table I. The distortion parameter, δ $(=1-c/a$, where a and c are the usual lattice parameters), shown in column 4, increases with increasing temperature.

The electric field gradient (EFG) at the indium site in the compound is axially symmetric about the crystal c axis,[1] and the EFG component along the c axis yields the parameter ϵ_0. The EFG at the site of the nucleus (designated by $\mathcal{E}$) and the EFG at the ion ($\mathcal{E}_0$) to which the nucleus belongs are related by the Sternheimer antishielding factor $(1-\gamma_\infty)$ through the relation.

$$\mathcal{E}=(1-\gamma_\infty)\mathcal{E}_0. \tag{1}$$

A recent calculation[7] of $(1-\gamma_\infty)$ for the In^{3+} ion yields a value of 25.9. This value is used in all calculations here. There are two contributions to the EFG in InBi: the ionic contribution ($\mathcal{E}_{0i}$) due to In^{3+} and Bi^{5+} ions situated at various lattice points, and the contribution arising from the nonuniform conduction-electron charge distribution ($\mathcal{E}_{0c}$). Thus

$$\mathcal{E}_0=\mathcal{E}_{0i}+\mathcal{E}_{0c}. \tag{2}$$

TABLE I. Lattice parameters and EFG in the intermetallic compound InBi as a function of temperature.

Temperature (°K) 1	a (Å) 2	c (Å) 3	Distortion parameter $\delta=1-c/a$ 4	ϵ_{0i} (10^{11} cgs esu) 5	$|\epsilon_{0\,\mathrm{expt}}$ (10^{11} cgs esu) 6
77	4.950	4.813	0.0277	−6.7720	15.1142
201	5.004	4.808	0.0391	−22.8181	7.1374
273	5.003	4.792	0.0424	−27.7300	22.3387
296	5.015	4.781	0.0470	−34.0888	30.3659

It is assumed in our calculations that all EFG sources are at an infinite distance from the core[8] and therefore that $(1-\gamma_\infty)$ is applicable to all sources. The quantity ϵ_{0i} at the indium site for each temperature has been calculated by the direct summation method, employing a FORTRAN program on a CDC 3600 computer. The summation was extended up to 30 000 neighboring atoms. The data are presented in column 5 of Table I, and they can be fitted by the equation

$$\mathcal{E}_{0i}=-171.31\times10^{14}\delta'/a^2c, \tag{3}$$

where $\delta'=\delta-0.023$. From the measured ν_Q at the site of the ^{115}In nucleus at these temperatures, the experimental value of EFG ($\mathcal{E}_{0\mathrm{exp}}$) has been evaluated using the nuclear quadrupole moment (1.161×10^{-24} cm^2) of ^{115}In nucleus measured by an atomic-beam experiment,[9] and the results are presented in column 6 of Table I.

DISCUSSION

A. Knight Shift

The salient features of the NMR experiment are the following: At lower temperatures, ν_Q at the site of the ^{115}In nucleus in the compound decreases with increasing temperature, vanishing at about 170°K, and then increasing with increasing temperature. The Knight shift of ^{115}In is negative at low temperatures, even with reference to the ^{115}In resonance in the most diamagnetic compound reported so far,[10] and the spectrum shifts to lower fields with increasing temperature, the Knight shift reaching zero at about 230°K. The Knight shift then increases smoothly in the positive direction with increasing temperature but abruptly doubles soon after the compound melts (Fig. 1). This is in contrast with the observations made in pure indium,[11] where K_{iso} remains unaltered even at 4.2°K, and there is no change in the shift on melting the metal.[4] The Knight shift for indium in the compound may be expressed as

$$K=K_{\mathrm{P}}+K_{\mathrm{L}}+K_{\mathrm{cp}}, \tag{4}$$

where K_{P}, K_{L}, and K_{cp} are the contributions to K due to Pauli paramagnetism of the s state of the conduction electrons (+ve), Landau diamagnetism of the conduction electrons (−ve) and core polarization resulting from the spins of the p-band electrons (usually −ve), respectively. A temperature-independent orbital contribution to K due to Kubo-Obata paramagnetism[12] (K_{orb}), which is usually small for nontransition metals,

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is neglected in Eq. (4). As the compound is highly diamagnetic this assumption is fairly valid. For most of the metals K_L is small compared to K_P, but, in some systems where the effective mass of the conduction electrons is very small, K_L is appreciable and may even dominate.[13] Bloembergen and Rowland[14] were the first to observe the negative Knight shift at the site of ^{205}Tl in the intermetallic compound NaTl. Even today this observation evokes great interest as this alloy does not contain any transition metal. Recently an attempt has been made by Bennett[15] to attribute the negative shift in NaTl to the large Landau diamagnetic contribution to K. Because of lack of data on effective mass of the conduction electrons in the compound, he could not calculate the exact contributions to K from K_P and K_L, but he feels that one need not invoke core polarization from p electrons to account for the observed shift. The negative Knight shift observed[16] at the site of ^{207}Pb in another intermetallic compound ($Na_{15}Pb_4$) containing nontransition elements has been attributed to core polarization.

In the intermetallic compound InBi the negative Knight shift at the site of the ^{115}In nucleus has been observed at low temperatures. The ratio of K_L and K_P is given by[13]

$$K_L/K_p = -\tfrac{1}{3}(m/m^*)^2/P_F\Delta\,, \tag{5}$$

where m is the free-electron mass, m^* is the effective mass of the conduction electrons in the compound, P_F is the average value of the electron-wave-function density at the nucleus, and Δ is the atomic volume. Since the electron wave function is normalized, P_F should be an inverse function of Δ. Under the free-electron approximation, $P_F\Delta$ for a given atom may be treated as a constant. Without invoking core polarization from p electrons, if one is to account for the observed negative shift $|K_L|>|K_p|$. In indium metal the total contribution to K_{iso} arising from K_L, K_{cp}, and K_{orb} is negligible[11] and the observed shift is mainly due to K_p. On this basis, from the observed K_{iso} in the metal, P_F at the indium nucleus for s-state electrons at the Fermi surface ($P_F=27.3\times10^{24}$ per cc) may be evaluated. In this calculation, the calculated value of χ_p from the electronic specific heat of indium metal[17] has been used. Assuming $P_F\Delta$ in the compound is the same as that in the metal, for the shift in the compound to be negative requires $m^*<0.022m$, whereas the effective masses of the conduction electrons in InBi for three different periods of oscillations determined by the de Haas–van Alphen (dHvA) effect[18] are 0.64m, 0.58m, and 0.21m. As the effective masses are greater by a factor of 10, any reasonable deviation of $P_F\Delta$ in the compound from the metal value cannot make $|K_L|$ greater than $|K_p|$. For $m^*\sim0.2m$, K_L will be only about 2% of K_p. As such, at least in InBi, the Landau diamagnetism cannot explain the observed negative shift and there must be an appreciable amount of core polarization from p-band electrons.

The electronic configurations of indium and bismuth atoms are $5s^25p^1$ and $6s^26p^3$, respectively, and therefore there are 16 electrons per unit cell (2 molecules per unit cell) in the InBi intermetallic compound. In the absence of overlapping of the Brillouin zones, one should expect the compound to behave as an insulator. But due to overlapping of the zones, there will be a few clusters of electrons in the next zone, leaving a few holes in the corners and the edges of the filled zones. The appearance of several sets of dHvA oscillations in the intermetallic compound[18] InBi confirms the Brillouin-zone–Fermi-surface interactions in the compound. The prediction of the small area of the Fermi surface in the compound is in conformity with the reported high electrical resistivity[19] and the observed small Knight shift and high bulk diamagnetic susceptibility (even after deducting the core contribution to the susceptibility, the sample remains diamagnetic close to the melting point). In short, the intermetallic compound InBi behaves as a divalent metal, and one should expect the variation of the Knight shift with respect to temperature if the c/a ratio varies with temperature[20] since it is well known that the variation of c/a alters the degree of overlapping of the Brillouin zones. In turn the change in the degree of overlapping will affect the relative percentage of s and p conduction electrons at the Fermi surface due to strong admixture of them at the Fermi surface. At room temperature, c/a of InBi is 0.953, and this ratio increases with decreasing temperature, leading to an increased overlapping of the zone in the axial direction with decreasing temperature. The observed negative shift at lower temperatures is understandable if the increase in overlapping of the zones at lower temperatures results in an increase in the relative percentage of p- to s-electron density at the Fermi surface. Since K_{ax} decreases with decreasing temperature, one may question the assumption of an increase in p-electron density at the Fermi surface with decreasing temperature. Since the distortion parameter (column 4 of Table I) decreases with decreasing temperature, one may not expect much contribution to K_{ax} from p electrons at the Fermi surface at lower temperatures. The flat portion of the Knight-shift curve in Fig. 1 around 150°K may be treated as a transition region below which the core polarization is a dominat-

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ing term, whereas at higher temperatures the direct hyperfine interaction due to s electrons at the Fermi surface is mainly responsible for the observed shift.

It has been pointed out[21] that the Knight shift versus susceptibility plot in transition metals (or alloys containing transition metals) gives rise to a negative slope if core polarization is responsible for the variation of the Knight shift with respect to temperature. In InBi, the positive slope of such a plot (Fig. 2) needs to be understood. In alloys containing transition metals, electrons at the Fermi surface in a narrow d band are responsible for the variation of the Knight shift and the susceptibility with respect to temperature. In InBi, the conduction electrons belong to s and p bands which are broad, and one should not expect any variation of the above type in the susceptibility and the Knight shift with respect to temperature. The variation observed in this compound is due to a different mechanism. It may be mainly due to Brillouin-zone–Fermi-surface interaction which is a function of c/a ratio. Without knowledge of the detailed electronic band structure in the compound, the numerical estimation of the susceptibility or the Knight shift is not possible. Nevertheless, an attempt has been made to understand the observed susceptibility qualitatively in the following way: Under the free-electron approximation the total conduction electron susceptibility due to Pauli paramagnetism and Landau diamagnetism is

$$\chi_{\text{cond}}\alpha[1-\tfrac{1}{3}(m/m^*)^2].$$

χ_{cond} is negative if $m^*\leq 0.6m$. As such χ_{cond} and hence the bulk susceptibility $(\chi_{\text{cond}}+\chi_{\text{core}})$ of the intermetallic compound InBi is diamagnetic since the effective mass of the conduction electrons in the compound[18] is $\lesssim 0.6m$. The substance becomes more and more diamagnetic as the number of electrons at the Fermi surface increases with decreasing temperature due to the increase in overlapping of the Brillouin zones along the c axis. In the foregoing discussion it has been assumed that all the electrons at the Fermi surface contribute to the torque oscillations of dHvA measurements and hence $m^*\lesssim 0.6m$. This is a reasonable assumption as we do not expect any larger pockets of conduction electrons at the Fermi surface in this compound. As already pointed out, the observed variation of the Knight shift with respect to temperature in the compound can also be understood if the increase in overlapping of the zones enhances the relative percentage of p- to s-electron density at the Fermi surface.

An abrupt variation in K at the melting point observed in this alloy is in conformity with our assumption that this alloy behaves like a divalent metal (a similar abrupt variation in K at the melting point has been observed in a divalent metal such as cadmium[20]).

A word of comment on the Knight shift in pure indium metal may be desirable. K_{iso} in the metal is large and insensitive to changes in c/a ratio. This is understandable as indium is a trivalent metal; with three valence electrons $(5s^25p^1)$, we expect one and a half Brillouin zones to be filled, giving a large area of Fermisurface in the second zone. The existence of a few electrons in the third or a few holes in the first zone are reported.[22] This may give rise to Brillouin-zone–Fermi-surface interaction. But its effect on the total area of the Fermi surface is negligible. Thus the density of states at the Fermi surface with s character, which mainly determines the amount of Knight shift, should be independent of c/a ratio.

B. Electric Field Gradient

Two serious attempts to account for the experimental ν_Q in indium metal have been reported.[23,24] The difference between the observed EFG and the calculated ionic contribution to the EFG is treated as the electronic contribution to EFG. Simons and Slichter[23] tried to attribute the conduction-electron contribution to the EFG to the p-state conduction electrons close to the nucleus. They postulate that the conduction-electron contribution to the EFG should be a linear function of δ, whereas the observed EFG as a function of temperature behaves differently. Hewitt and Taylor[24] attempted to explain the conduction-electron contribution to the EFG by introducing "a modest amount of an undulatory component of electronic charge density having the periodicity of the lattice." In their calculation a parameter ζ is incorporated to specify the amplitude of undulation. Although ζ assumes reasonable values to account for the observed EFG at various temperatures in indium metal, it appears to be temperature-dependent.

The experimental EFG in InBi intermetallic compound presented in the last column of the table may assume one of the following four possible signs: (i) positive throughout the temperature range studied, (ii) negative in the same range, (iii) positive at the temperature above 168°K and negative below that temperature, and (iv) vice versa. All four possibilities have been considered for determining the conduction-electron contribution to the EFG, and it is found that none of them gives rise to a reasonable contribution to the EFG as a function of the distortion parameter of the lattice δ or δ'.

We have not made any detailed calculation for InBi to determine the amount of undulatory component of electronic charge density to be introduced to account for the observed EFG by the method outlined by Hewitt and Taylor.[24] A preliminary calculation showed that this method would not help us in understanding the observed EFG in InBi intermetallic compound. As

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usual, the electronic contribution to the EFG in this compound, as in the pure metal,[11] needs to be explained by some other mechanism.

CONCLUSION

We expect that the Fermi-surface in the intermetallic compound InBi is dominated by p electrons, and that the Brillouin zones are almost completely full with a few electrons spilling to the higher zones. It has been shown that K_{cp} is responsible for the observed Knight shift at low temperatures. The observed EFG at the site of the ^{115}In nucleus could not be explained, even qualitatively, by any known mechanism.

As the observed variations of the susceptibility and the Knight shift with respect to temperature depend to some extent upon the effective mass of the conduction electrons in the compound, it will be interesting and helpful in interpreting the NMR data if m^* can be obtained in the compound at various temperatures.

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Magnetic Properties of Dilute Gold-Vanadium Alloys: Nuclear Magnetic Resonance in *Au*V and *Au*(Ag)V

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The low-temperature (1–4°K) magnetic properties of dilute (0.1–10 at.%) *Au*V alloys have been studied by means of pulsed-NMR techniques. The previously reported ^{51}V line-shape anomaly for vanadium concentrations near 1 at.% is shown to result from a large reduction in the vanadium spin susceptibility for vanadium impurities that are nearest neighbors to each other. The observed change in the ^{51}V resonance shift from a negative value (-1.5%) at low vanadium concentrations to a positive value ($+0.6\%$) at high concentrations is consistent with the expected variation in the ratio of "nonmagnetic" to "magnetic" vanadium concentrations. The nuclear resonances are severely broadened as a result of oscillatory spin-density disturbances associated with d-resonance scattering of the host conduction electrons. There is no indication, however, that the field-induced impurity magnetization gives rise to significant long-range negative-definite spin polarizations in the host metal as suggested recently. This conclusion is supported by the absence of positive ^{109}Ag resonance shifts in ternary *Au*(Ag)V alloys containing up to 20 at.% silver. In general, our measurements suggest that "magnetic" as well as "nonmagnetic" vanadium sites can be described by a virtual bound d-state model in which the impurity susceptibility, resonance shift, and nuclear-spin relaxation rates are enhanced by local Coulomb interactions. The two types of vanadium sites are distinguished by different enhancement factors, or, equivalently, different spin-fluctuation frequencies. The ^{51}V spin-lattice relaxation rates T_1^{-1} are directly proportional to the absolute temperature over the entire composition range. In the infinite-dilution limit $T_1T\approx 17$ msec°K, while at high concentrations T_1T approaches the metallic vanadium value. An analysis of the infinite-dilution ^{51}V shift and relaxation-rate data indicates that the impurity-site spin susceptibility accounts for most of the measured bulk susceptibility.

I. INTRODUCTION

The anomalous low-temperature properties of many dilute solid solutions of transition-element impurities in nonmagnetic host metals have stimulated considerable experimental and theoretical work during recent years.[1] In particular, much effort has been aimed at elucidating the origin of the well-known resistance minimum and associated magnetic phenomena in metals containing paramagnetic impurities. The traditional approach to these problems has been to assume the existence of a localized magnetic moment at the impurity site and to treat the interaction between the impurity spin ($\mathbf{S}$) and the conduction-electron spins ($\boldsymbol{\sigma}$) by means of an isotropic s-d exchange term $-2J\mathbf{S}\cdot\boldsymbol{\sigma}$. Using perturbation theory, Kondo[2] discovered that the s-d interaction leads in the second Born approximation

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