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Susceptibilities and Negative Knight Shifts of Intermetallic Compounds

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Knight shift measurements have recently been made on a series of compounds having the β-wolfram structure V_3X, namely V_3As, V_3Au, V_3Ga, V_3Ge, V_3Pt, V_3Sb, V_3Si, and V_3Sn. More recently susceptibilities have been measured on some of these compounds. It is observed that (a) materials with a high superconducting transition temperature show temperature-dependent Knight shifts and susceptibilities, (b) the vanadium shifts K_V are positive and decrease with decreasing temperature, and (c) the X-site shifts K_X are negative and increase in magnitude with decreasing temperature. A simple model is offered which uses the exchange polarization mechanism to relate the sign and temperature dependence of K_V and K_X to the temperature-dependent susceptibility.

INTRODUCTION

RECENTLY an extensive experimental investigation of nuclear magnetic resonance (NMR) properties of intermetallic compounds has been made.[1,2] From certain of these experiments, correlations have been found between the NMR properties and superconductivity in binary vanadium compounds having the β-wolfram structure (see Fig. 1) V_3X, where $X=$ As, Au, Co, Ga, Ge, Si, Sb, Sn, and Pt. Measurements were made of the Knight shift K_V at the V site and, where possible, of the shift K_X at the X site. In the usual way K was obtained by comparing the change in the field for resonance in the metal relative to a diamagnetic insulating solid or liquid. On some of these compounds measurements have more recently been made of the temperature dependence of the susceptibility.[3] The latter results are presented in Fig. 2.

There are a number of striking features of the measurements presented in reference 1 and in Fig. 2 which we list below:

(a) Only those materials that have a high superconducting transistion temperature T_s show strongly temperature-dependent Knight shifts and susceptibilities.

(b) K_V is *positive* and, in the superconductors, decreases with decreasing temperature.

(c) K_X is *negative* and, in the superconductors, its magnitude increases with decreasing temperature.[4]

(d) The susceptibility increases with decreasing temperature in the superconductors.

We offer below a simple theory which gives a consistent account of these observations.

THEORY

According to the usual picture, the Knight shift in metals arises from the contact hyperfine interactions between the nuclear magnetic moment and the field arising from the net spin moment of the conduction electrons. The theory of Townes, Herring, and Knight[5] predicts that

$$K=(8\pi/3)\chi_p\Omega\langle|\psi_s(0)|^2\rangle_F, \tag{1}$$

where χ_p is the spin susceptibility per unit volume, Ω is the volume of the unit cell, and $\langle|\psi_s(0)|^2\rangle_F$ is the average value of s conduction electron probability density at the nucleus for electrons near the Fermi surface. The Pauli spin susceptibility χ_p is positive and essentially temperature independent. It is expected therefore that K should be positive and independent of temperature. For the great majority of primary metals and binary alloys for which NMR studies have been made, this is the case. Equation (1) is often alternatively expressed in terms of the free-atom hyperfine field H_{hf} per spin by the relation

$$K=(M_0/2\mu_B)H_{\mathrm{hf}}\chi A\xi, \tag{2}$$

where M_0 is the mass of an atom of unit atomic weight, μ_B is the Bohr magneton, χ is the susceptibility per gram, A is the atomic weight, and ξ is the ratio of $|\psi(0)|^2$ in the metal to its value in the free atom.

To account for the observations listed above we must modify the simple theory. We shall assume that in the V_3X compounds, there is a conduction band formed principally from vanadium $4s$ and $4p$ wave functions which overlaps a narrower band formed mainly from the vanadium $3d$ wave functions. We suppose that both these bands are cut by the Fermi surface. We also assume that the ns wave functions belonging to the X site form a very narrow band lying far below the Fermi surface. This assumption reflects the fact that the X atoms are distant from one another so that their levels will be broadened only to the extent that they mix with the intervening vanadium wave functions. Finally, we assume that the np wave functions belonging to the X site lie sufficiently close to the Fermi surface so that

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[1] W. E. Blumberg, J. Eisinger, V. Jaccarino, and B. T. Matthias, Phys. Rev. Letters **5**, 149 (1960). It is the interpretation of these results which concerns us in the present paper. [Previous measurements of the Ga and Sn Knight shifts in V_3Ga, Nb_3Ga, V_3Sn, and Nb_3Sn have been reported; see R. G. Shulman, B. J. Wylnda, and B. T. Matthias, Phys. Rev. Letters **1**, 278 (1958).]

[2] V. Jaccarino, B. T. Matthias, M. Peter, H. Suhl, and J. H. Wernick, Phys. Rev. Letters **5**, 251 (1960). The magnitude and sign of the Knight shifts observed in these rare earth metals is of different origin from that which concerns us in the V_3X metals.

[3] H. J. Williams and R. C. Sherwood, Bull. Am. Phys. Soc. Ser. II **5**, 430 (1960).

[4] K_{Co} is positive in V_3Co and forms an exception to this rule. As will be seen later, this behavior can be understood within the framework of the theory.

[5] C. H. Townes, C. Herring, and W. D. Knight, Phys. Rev. **77**, 852 (1950).

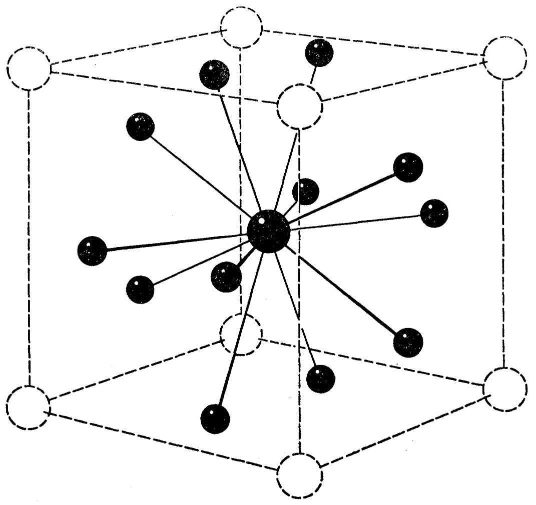

FIG. 1. The β-wolfram structure: space group $Pm3n$. In the compound V_3X the X atoms, at body-centered cubic positions, have 12 V nearest neighbors at a distance $\frac{1}{4}\sqrt{5}a_0$ and 8 X next nearest neighbors at $\frac{1}{2}\sqrt{3}a_0$. The nearest neighbors to a V atoms are two other V atoms only $\frac{1}{2}a_0$ distant.

they are strongly admixed with the vanadium bands. This band structure is shown *very* schematically in Fig. 3.

This model of the band structure accounts for the NMR properties of the vanadium nucleus in V_3X as follows: The susceptibility of the conduction band may be expressed as the sum of s- and d-band susceptibilities; $\chi=\chi_s+\chi_d$. The temperature-independent susceptibility χ_s will produce a contribution to K_V that is positive and constant in accordance with Eq. (2). Since no contact hyperfine interaction is expected for d electrons, a contribution to K_V from χ_d may arise only from exchange polarization of inner s-shell electrons by the d electrons as has been shown by Heine and Wood and Pratt.[6] The contribution from this mechanism to K_V is negative. Since K_V decreases, with decreasing temperature, while the susceptibility increases, we must assume that the increase in χ is caused by an increase in χ_d.

A similar explanation accounts for the NMR properties of the X nucleus. We have assumed that the ns electrons belonging to this site are in a narrow band far below the Fermi surface. This band will therefore be filled and cannot contribute to the observed shifts. We have assumed, however, that the $X-np$ electrons are in a band strongly admixed with the vanadium bands. Any polarization of the compound will consequently represent a partial polarization of these electrons. However, just as for d electrons, the p electrons have no contact hyperfine interaction. Although no exchange polarization calculations have been made for the present case, we shall introduce experimental evidence below to show that this interaction exists and is such as to explain the negative Knight shifts for the atoms occupying X sites in the V_3X compounds. A similar situation has been discussed by Cohen, Goodings, and Heine.[7] We expect therefore, a negative contribution to the Knight shift from both the s and d Fermi surfaces accounting for the fact that the shift at the X site is uniformly negative. In those compounds where χ increases with decreasing temperature, the shift will become more negative at lower temperatures.

In the special case of V_3Co, the similarity of the energy levels of V and Co will evidently lead to a $4s$ electron spin density at the Co nucleus. It is not surprising that K_{Co} is positive in V_3Co in contrast to all other V_3X compounds studied.

Based on the above model of the band structure of the V_3X compounds, we shall write for the Knight shifts K_V and K_X at the two sites

$$K_V=\xi_V\alpha\chi_s-\eta_V\beta\chi_d, \qquad (3)$$

$$K_X=-\xi_X\gamma\chi_s-\eta_X\gamma\chi_d, \qquad (4)$$

where χ_s and χ_d are the susceptibilities per gram for the s and d Fermi surfaces; $(\xi_V+\xi_X)$ and $(\eta_V+\eta_X)$ are numbers of order unity; and α, β, and γ are given in accordance with Eq. (2) by the relations

$$\alpha=\frac{M_0}{2\mu_B}(M_V+\tfrac{1}{3}M_X)H_{\text{hf}}(\text{vanadium } s \text{ electron}), \qquad (5)$$

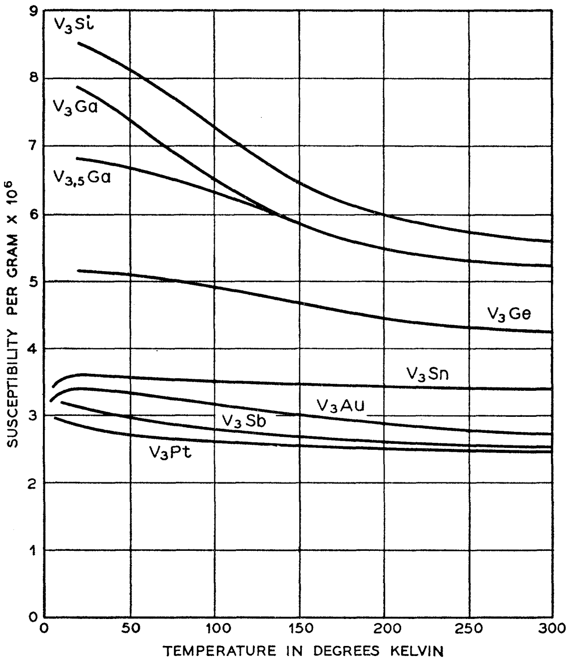

FIG. 2. Measurements made by Williams and Sherwood of the temperature dependence of the susceptibility of some of the V_3X compounds. The superconducting transition temperatures are for $V_3Si-17.1$; $V_3Ga-16.5$; $V_{3.5}Ga-13.4$; $V_3Ge-6.0$, $V_3Pt-2.8$; $V_3Sn-<1$; $V_3Au-<1$; and $V_3Sb<1$ (all in °K).

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[6] V. Heine, Phys. Rev. **107**, 1002 (1957); J. H. Wood and G. W. Pratt, Jr., Phys. Rev. **107**, 995 (1957).

[7] M. H. Cohen, D. A. Goodings, and V. Heine, Proc. Phys. Soc. (London) **A73**, 811 (1959).

$$\beta=\frac{M_0}{2\mu_B}(M_{\mathrm{V}}+\tfrac{1}{3}M_X)H_{\mathrm{hf}}(\text{vanadium } d \text{ electron}), \quad (6)$$

$$\gamma=\frac{M_0}{2\mu_B}(M_X+3M_{\mathrm{V}})H_{\mathrm{hf}}(X\ p \text{ electron}). \quad (7)$$

Here M_{V} and M_X are the atomic weights of the vanadium and X atom, respectively, and $M_0/2\mu_B=0.895\times10^{-4}$ cgs units. [A derivation of Eqs. (5), (6), and (7) is given in the Appendix.] These coefficients are evaluated in Table I. The hyperfine fields used in this table are taken from various sources. H_{hf} (vanadium s electron) is obtained from the Fermi-Segrè formula[8] using the term values for the V configuration $3d^44s^1$. H_{hf}(vanadium d electron) is calculated from experimental values of A^{51} obtained from electron paramagnetic resonance experiments on the V^{++} ion. $H_{\mathrm{hf}}(X\ p$ electron) comes from atomic beam and other measurements of the hyperfine structure of P, As, and Sb atoms.[9] These atoms have in common a half-filled p shell and a ground state $^4S_{\frac{3}{2}}$. Because the p electrons couple to give $L=0$, the orbital and dipolar contributions to the hfs interactions vanish. Since no contact hfs is to be expected for p electrons, it was originally believed that no hfs would be observed for these atoms. In actual fact, there is considerable hfs present in each case, presumably due to the exchange polarization effect. We have assumed in these calculations that the hyperfine field per spin is the same for P and Si; for As, Ge, and Ga; and for Sb and Sn, respectively.

It is clear from Eqs. (3) and (4) that an important consequence of the hypothesis offered above is that K_{V} and K_X should be linear functions of the total susceptibility. In Figs. 4 and 5 we have plotted Knight shifts against susceptibility for the superconductors V_3Si, V_3Ge, and V_3Ga. A linear relation is followed closely in all cases for the shifts at both sites, confirming the expected relation. It is particularly interesting that the data for V_3Ge lie closely along the same line defined by V_3Ga, even though the superconducting transition temperatures vary widely. It appears therefore that the important difference between these compounds is their susceptibility, and that the other constants entering Eqs. (3) and (4) are nearly equal as predicted in Table I.

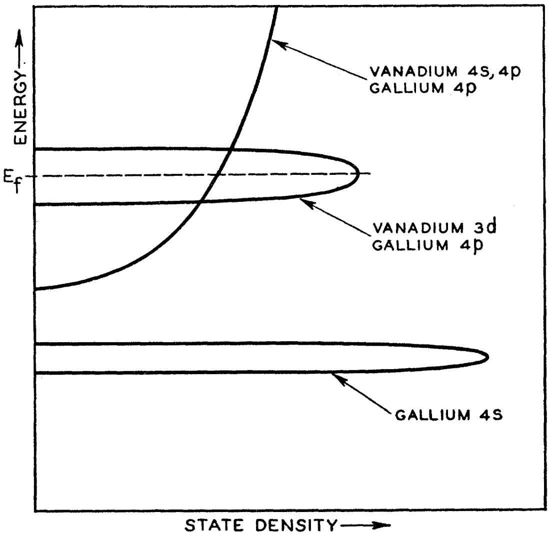

FIG. 3. A schematic diagram indicating the density of states vs energy for V_3Ga illustrating the band structure assumed in the text.

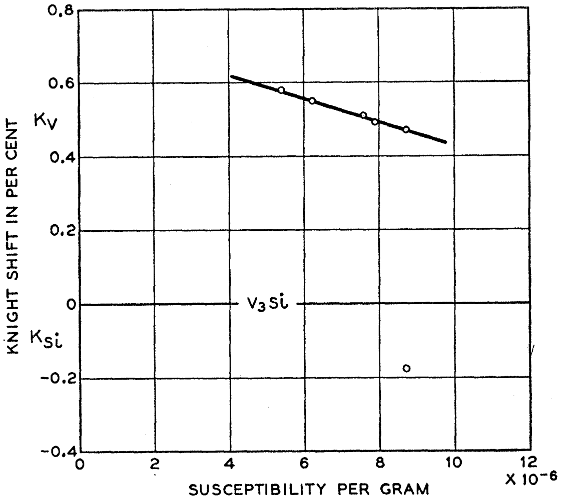

FIG. 4. The Knight shift of V^{51} and Si^{29} in V_3S vs susceptibility. K_{Si} has been measured at but one temperature.

The slopes of the straight lines in Figs. 4 and 5 determine the quantities $\eta_{\mathrm{V}}\beta$ and $\eta_X\gamma$. Using data from Table I we can calculate η_{V} and η_X with results shown in Table II. The fact that the value obtained for $(\eta_{\mathrm{V}}+\eta_X)$ is of order unity supports our assumption about the origin of the negative contributions to the Knight shift.

Since K_{V} and K_X are both linear functions of the susceptibility, they must also be linearly related to each other. In Fig. 6 we have plotted K_X against K_{V} for V_3Ga and V_3As. The points for different temperatures and different compounds are seen to cluster closely around a common straight line. An equation for this line can be obtained by eliminating χ_d between Eqs. (3) and (4),

$$\frac{K_{\mathrm{V}}}{\eta_{\mathrm{V}}\beta}-\frac{K_X}{\eta_X\gamma}=\left(\frac{\xi_{\mathrm{V}}\alpha}{\eta_{\mathrm{V}}\beta}+\frac{\xi_X}{\eta_X}\right)\chi_s. \quad (8)$$

As we pass from the As group of compounds to the P and Sb groups, the ratio α/β does not change. If we assume as a rough approximation that ξ_{V}, ξ_X, η_{V}, η_X and $\beta\chi_s$ do not change appreciably, we can use Eq. (8) and the values of γ given in Table I to predict straight lines for the P and Sb groups. These lines are drawn in Fig. 7 together with the available data, which are clearly consistent with the predictions.

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[8] E. Fermi and E. Segrè, Z. Physik **82**, 729 (1933).

[9] These results are given by R. L. Christensen, thesis, Princeton University, 1957 (unpublished).

TABLE I. Hyperfine interaction coefficients for certain V_3X compounds.

Compound	$M_V+\frac{1}{3}M_X$	M_X+3M_V	H_{hf}(oe) vanadium s per spin	H_{hf}(oe) vanadium d per spin	H_{hf}(oe) X p per spin	α	β	γ
V_3Si	60.3	180.9	3.2×10^6	-2.34×10^5	-1.87×10^4	7900	1260	303
V_3As	75.9	227.8	3.2×10^6	-2.34×10^5	$-8.7\ \times10^4$	9900	1590	1780
V_3Ge	75.2	225.5	3.2×10^6	-2.34×10^5	$-8.7\ \times10^4$	9800	1570	1760
V_3Ga	74.2	222.6	3.2×10^6	-2.34×10^5	$-8.7\ \times10^4$	9700	1550	1740
V_3Sb	91.5	274.6	3.2×10^6	-2.34×10^5	$-29.3\ \times10^4$	11 900	1920	7210
V_3Sn	90.5	271.6	3.2×10^6	-2.34×10^5	$-29.3\ \times10^4$	11 800	1890	7100

DISCUSSION

The most important implication we draw from the considerations outlined above is that the NMR properties of the V_3X compounds are essentially a consequence of the dependence of the susceptibility upon temperature. The correlations that have been observed[1] between the NMR properties and the superconducting transition temperature T_s reflect the fact that superconductivity in the V_3X compounds is correlated with a temperature-dependent susceptibility. Since the NMR results indicate that the temperature-dependent component of the susceptibility is due to vanadium d electrons, the correlation appears to exist chiefly between superconductivity and temperature dependence of the d-band susceptibility.

One possible interpretation of the temperature dependence of the susceptibilities plotted in Fig. 2 is that a sharp peak exists in the density-of-states curve for the d band, and that the Fermi level intersects this peak in the superconductors. Let us suppose that there is a contribution to the density of states in the d band which has the form

$$\eta(E)=\eta(E_F)\left[1-\frac{(E-E_f)^2}{\epsilon^2}\right], \tag{9}$$

if $E_f+\epsilon\leq E\leq E_f-\epsilon$, and elsewhere zero. Then the contribution to the susceptibility is given by

$$\rho\Delta\chi=4\mu_B{}^2\eta(E_F)\int_0^1 y\tanh\left(\frac{\epsilon}{2kT}y\right)dy, \tag{10}$$

where $\Delta\chi$ is susceptibility per gram, and ρ is the density. Using Eq. (10), a very good fit can be made to the susceptibility curves of V_3Si and V_3Ga in Fig. 2 with the constants given in Table III. In Table III, $\rho\chi_0=2\mu_B{}^2\eta(E_F)$ and χ_∞ is the constant component of the susceptibility. It is interesting to notice how extremely narrow a peak is required in the density of states to account for the temperature dependence of χ in this way. A width of 500°K corresponds to about 0.04 ev which is much finer structure than is normally expected to occur in a density of states distribution. We may speculate that such a peak in density of states, if it actually exists, could be associated with the particular crystal structure of the V_3X compounds which tends to isolate the X-site atoms from each other.

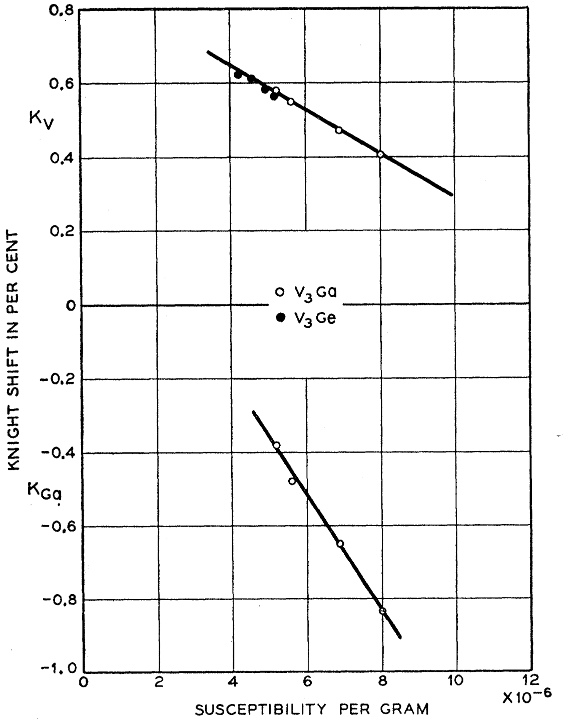

FIG. 5. The Knight shift of V^{51} and $Ga^{69,71}$ in V_3Ga and V^{51} in V_3Ge vs susceptibility.

In connection with the occurrence of superconductivity in the V_3X compounds, the following calculation may be significant. If χ_m is the maximum susceptibility of a particular compound at $T=0$, and η_m is the corresponding density of states, then we have the relation $\rho\chi_m=2\mu_B{}^2\eta_m$, where ρ is the density. If 2ϵ is the width of the peak in density of states, we may easily calculate the number of electrons per unit volume required to fill all states in the peak to be

$$\Delta n=(\rho\chi_m/\mu_B{}^2)2\epsilon.$$

This result may also be expressed as the number of electrons per unit cell $\Delta N=\Omega\Delta n$,

$$\Delta N=(M_0/\mu_B{}^2)(6A_V+2A_X)\chi_m 2\epsilon.$$

We have $M_0/\mu_B{}^2=1.93\times10^{16}$. For V_3Ga, $(6A_V+2A_{Ga})=445$, $\chi_m=8.0\times10^{-6}$, and $2\epsilon=400°K=5.5\times10^{-14}$ erg. We obtain therefore $\Delta N=3.78$ per unit cell or 1.9 per

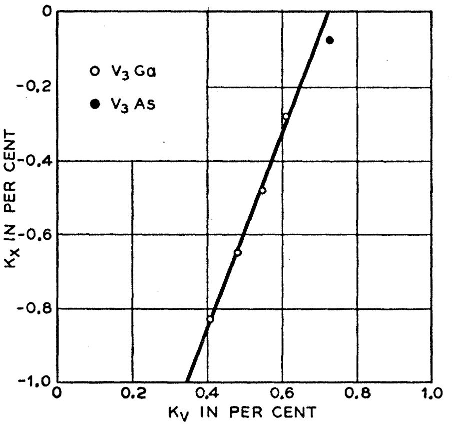

FIG. 6. The Knight shift K_V vs the Knight shift K_X in two V_3X compounds: V_3Ga and V_3As. The different points for a given compound correspond to measurements made at different temperatures.

Ga site. If Ga is presumed to be near the peak of the density of states curve, then about one extra electron per Ga site should fill the states to beyond the peak. This is not inconsistent with the fact that a sharp drop in transition temperature is observed in going from V_3Ga to V_3Ge.

We have interpreted the origin of the negative Knight shift at the Ga site, say, in V_3Ga to be a consequence of the fact that the Ga $3p$ band is strongly mixed with the V conduction band while the Ga $3s$ band is not. One could equally well expect a situation in which the p as well as the s band lies far below the Fermi surface, in which case zero Knight shift would be expected. This is indeed the case in Nb_3Ga which is isostructural with the V_3X compounds and is, by the way, a superconductor.[1]

TABLE II. Values of η_V and η_X for certain V_3X compounds.

Compound	$\Delta K_V/\Delta\chi$	$\Delta K_X/\Delta\chi$	η_V	η_X	$\eta_V+\eta_X$
V_3Ga	600	1600	0.39	0.92	1.31
V_3Ge	600		0.38		
V_3Si	320		0.25		

That physical isolation of the atoms may not be a prerequisite for observing a negative Knight shift in an intermetallic compound is suggested by the unusual properties of NaTl in which a large, negative K_{Tl} was observed.[10] (This was the first negative Knight shift observed.) In this peculiar structure the eight nearest neighbors of a Tl atom are four Na and four Tl atoms each of which separately form a diamond-like lattice. Now the atomic configuration for Tl is $6s^26p$ and for bismuth, the corresponding half-filled p shell atom, $(6s^26p^3)$ we have, again, a large negative hyperfine field.[9]

TABLE III. Constants determined by using Eq. (10) to fit the susceptibility data.

Compound	χ_0	χ_∞	$2\epsilon/k$ (°K)	T_s (°K)
V_3Si	4.3×10^{-6}	4.4×10^{-6}	500	17.1
V_3Ga	3.7×10^{-6}	4.4×10^{-6}	400	16.5

We presume then that the band structure of this intermetallic compound is such that the s electrons do not contribute to the conductivity while the p electrons do, resulting in a negative K_{Tl}.

ACKNOWLEDGMENTS

We are particularly indebted to H. J. Williams and R. C. Sherwood for permission to use the susceptibility measurements given in Fig. 1 without which the detailed interpretations made in this paper would not have been possible. We would like to thank L. R. Walker for several informative discussions.

APPENDIX

We suppose that the unit cell of a crystal contains atoms located at points 1, 2, 3, $\cdots$. A wave function centered at point 1 in the nth cell will be written $\psi_1(\mathbf{r}-\mathbf{r}_n)$. The tight-binding wave function constructed from these individual functions may then be written as

$$\psi=\frac{1}{\sqrt{N}}\sum_n e^{i\mathbf{k}\cdot\mathbf{r}_n}[a_1\psi_1(\mathbf{r}-\mathbf{r}_n)+a_2\psi_2(\mathbf{r}-\mathbf{r}_n)+\cdots], \quad \text{(A1)}$$

where N is the number of cells and $a_1^2+a_2^2+\cdots=1$. In an obvious extension of Eq. (2), the Knight shift at site

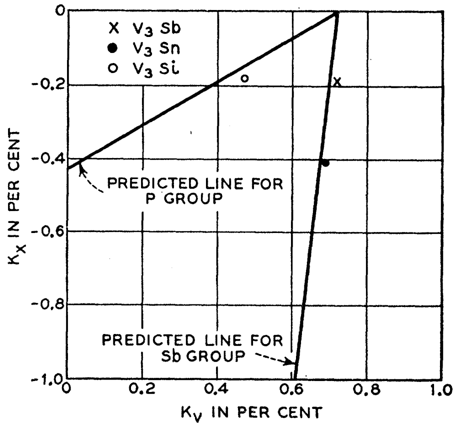

FIG. 7. The Knight shift K_V vs the Knight shift K_X in three V_3X compounds; V_3Sb, V_3Sn, and V_3Si. The straight lines are those predicted from the theory given in the text.

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[10] N. Bloembergen and T. J. Rowland, Acta Met. 1, 73 (1953).

X is given by

$$K_X=\frac{M_0}{2\mu_B}(H_{\rm hf})_X\chi(A_1+A_2+\cdots)\xi_X a_X^2, \qquad \text{(A2)}$$

where A_1, A_2, $\cdots$ are the atomic weights of the atoms at the respective sites, and ξ_X is the ratio of the hyperfine field at site X in the metal to its value in the free atom. The sum $\sum_X \xi_X a_X^2$ should be a number of order unity.

For V_3X, the unit cell contains six V atoms and two X atoms. From Eq. (A2) we have

$$K_V=\frac{M_0}{2\mu_B}(H_{\rm hf})_V\chi(A_V+\tfrac{1}{3}A_X)(6a_V^2\xi_V), \qquad \text{(A3)}$$

$$K_X=\frac{M_0}{2\mu_B}(H_{\rm hf})_X\chi(3A_V+A_X)(2a_X^2\xi_X), \qquad \text{(A4)}$$

with $(6a_V^2\xi_V)+(2a_X^2\xi_X)\simeq 1$. With some changes in notation this is the result used in the text.

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Fine Structure of Secondary Emission vs Angle of Incidence of the Primary Beam on Titanium Single Crystals*

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The secondary emission ratio of single crystals of titanium has been measured as a function of the angle of incidence of the primary electron beam. The curves show a general increase of the secondary emission ratio with increasing angle between the electron beam and the normal to the crystal face. Superimposed upon this general increase are a number of small relative maxima. The larger and broader of these maxima occur whenever the primary beam is incident along one of the major zone axes of the crystal. The magnitudes of these bands vary with the energy of the incident electrons, but their angular position is independent of energy. The smaller, extremely narrow bands do not correspond to major zone axes of the crystal. Both the magnitude and angular position of these latter peaks vary with the primary energy. The origin of these bands is explained in terms of diffraction of the incident electrons by the crystal lattice.

INTRODUCTION

THE curves of the secondary emission ratio, δ, of titanium crystals vs the angle, θ, between the primary beam and the normal to the crystal surface show fine structure superimposed on a smooth variation. This fine structure appears when the primary beam is directed approximately along a principal zone axis, and its angular position is independent of the energy of the primary electrons. This type of effect was first discovered on MgO crystals by Laponsky and Whetten.[1] The data on titanium also show smaller, narrower peaks, called ultrafine structure, whose angular position varies with primary energy. The structure in the curves was studied for angles of incidence up to ±60° and for primary energies from 120 ev to 10 kev. It appears that both the "normal" fine structure and the ultrafine structure can be explained in terms of diffraction of the primary electrons in the surface layers of the crystal.[2]

I. EXPERIMENTAL PROCEDURE

The magnitudes of the peaks in the curves of δ vs θ range from the order of 1% to 20% of the total secondary yield. Thus, in order to obtain precise quantitative data on the magnitude, width, and position of these peaks it is necessary to measure the total yield with considerable accuracy. The basic electron circuit which is employed in these measurements is shown in Fig. 1. The primary beam, I_p, leaving the electron gun passes through a small hole in the collector and strikes the target, producing secondary electrons. The secondaries are emitted at all angles and have energies ranging from zero to that of the primary electrons. When the collector is at a positive potential with respect to the target, all of the secondaries are collected and the ratio of I_c to I_p is the total secondary emission ratio which we represent by "δ". When the bridge circuit in Fig. 1 is balanced, the ratio of I_c to I_p is proportional to the value of the setting on the ten-turn potentiometer (for values of δ not exceeding 2), and thus can be determined quite accurately.

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* Based on a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy to the University of Minnesota in December 1959. Supported by the Electronics Components Laboratory of the Wright Air Development Center.

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[1] A. B. Laponsky and N. R. Whetten, Phys. Rev. Letters **3**, 510 (1959).

[2] A. J. Dekker, Phys. Rev. Letters **4**, 55 (1960).