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Effect of Low-Temperature Structural Transformation on V^{51} Knight Shifts and Electric Field Gradients in V_3Si

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The nuclear magnetic resonance of V^{51} in V_3Si has been observed in the presence of the low-temperature V_3Si structural transformation. Both the nuclear-electric-quadrupolar interactions and the Knight shift of the field for resonance are affected by the transformation, with two distinguishable vanadium sites evolving. The nuclear resonance resolves values of $e^2qQ=2.674$ MHz and 3.262 MHz and Knight shift 0.41% and 0.45% for field perpendicular to the vanadium symmetry axis for the two sites, respectively. The changes result from changes in the electronic structure, the observed field-gradient change being some sixty times greater than the relative change in the point-charge contribution to the field gradient. The measurements were made in polycrystalline material, and present a means of detecting structural transformations in polycrystalline metals. The effects of possible further distortions within the unit cell are considered.

I. INTRODUCTION

NUCLEAR magnetic resonance (NMR) measures the magnetic and electrostatic interactions of nuclei with the electrons of their surroundings. Thus, NMR studies of V_3Si and related intermetallic compounds were quite useful in determining the role of spin and orbital mechanisms in the magnetic behavior of these materials.[1] Electric quadrupole interactions of the nuclei were also found to be strongly dependent on the electronic structure of the material.[2] More recently, it was found that V_3Si undergoes a low-temperature structural transformation several degrees above its superconducting transition temperature. We have studied the effect of this transformation on the NMR properties. By virtue of the atomic character of the measurements, we have been able to make local measurements of the Knight shift and electric quadrupole interaction, and to distinguish between different vanadium sites with distinct Knight shifts, magnetic susceptibilities, and electric field gradients which develop in the transformation.

Evidence of a transformation near 20°K in V_3Si was first found by neutron-diffraction techniques. More thorough examination by x-ray diffraction[3] indicated that on cooling, the cubic structure of V_3Si transformed to a tetragonally distorted structure with $c/a\cong1.0024$. A marked low-temperature softening of V_3Si against 110 shear-wave strains was also found.[4] Effects on the phonon spectrum and connection with the high-superconducting transition temperature (17.1°K) suggested themselves. It has thus been of special interest to measure the NMR quantities which bear on changes in the electronic structure which accompany changes in the crystal structure.

II. EXPERIMENT

Since not all V_3Si undergoes a complete spontaneous transformation on cooling, it is important to obtain material which transforms as completely as possible. The residual resistance is the most reliable criterion for complete transformation, samples with high residual resistance ratios transforming most completely.[5] A zone-melted polycrystalline ingot of resistance ratio 33 (between 300 and 0°K) was used in the measurements reported here.[6] In order to achieve rf penetration of the sample, the ingot was shattered with a mortar and pestle and passed through a 100-mesh screen. The experiments were performed on the material that passed the screen. Earlier experience indicated that V_3Si and similar intermetallic compounds are sufficiently brittle that the action of the mortar and pestle leads to fracture of the material rather than strain. Passing the material through a 100-mesh screen rather than the customary 400-mesh screen reduced the amount of crushing necessary.

The sample was placed in the crossed rf coils of a Varian wideline NMR spectrometer and its resonance studied by conventional techniques. The nuclear resonant absorption derivative was measured by recording the nuclear induction response to a 6-Oe (peak-to-peak) 400-Hz modulating field superimposed on a slowly swept dc magnetic field. An rf field of approximately 0.5 Oe at 16 MHz was used. Temperatures below 20.2°K were obtained by immersing the sample in pumped liquid hydrogen. Temperatures above 20.2°K where obtained by placing the sample in a heated vial machined from a single crystal of quartz. The single-crystal quartz, because of its high thermal conductivity, formed an isothermal enclosure which, being an elec-

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[1] A. M. Clogston and V. Jaccarino, Phys. Rev. **121**, 1357 (1961); A. M. Clogston, A. C. Gossard, V. Jaccarino, and Y. Yafet, Phys. Rev. Letters **9**, 262 (1962).

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[3] C. G. Shull, MIT Annual Report—Research in Materials Science, 1963–1964 (unpublished); B. W. Batterman and C. S. Barrett, Phys. Rev. Letters **13**, 390 (1964).

[4] L. Testardi, T. B. Bateman, W. A. Reed, and V. G. Chirba, Phys. Rev. Letters **14**, 537 (1965).

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[6] The resistance measurements were made by E. J. Ryder at Bell Telephone Laboratories. The zero-degree value was obtained by extrapolation.

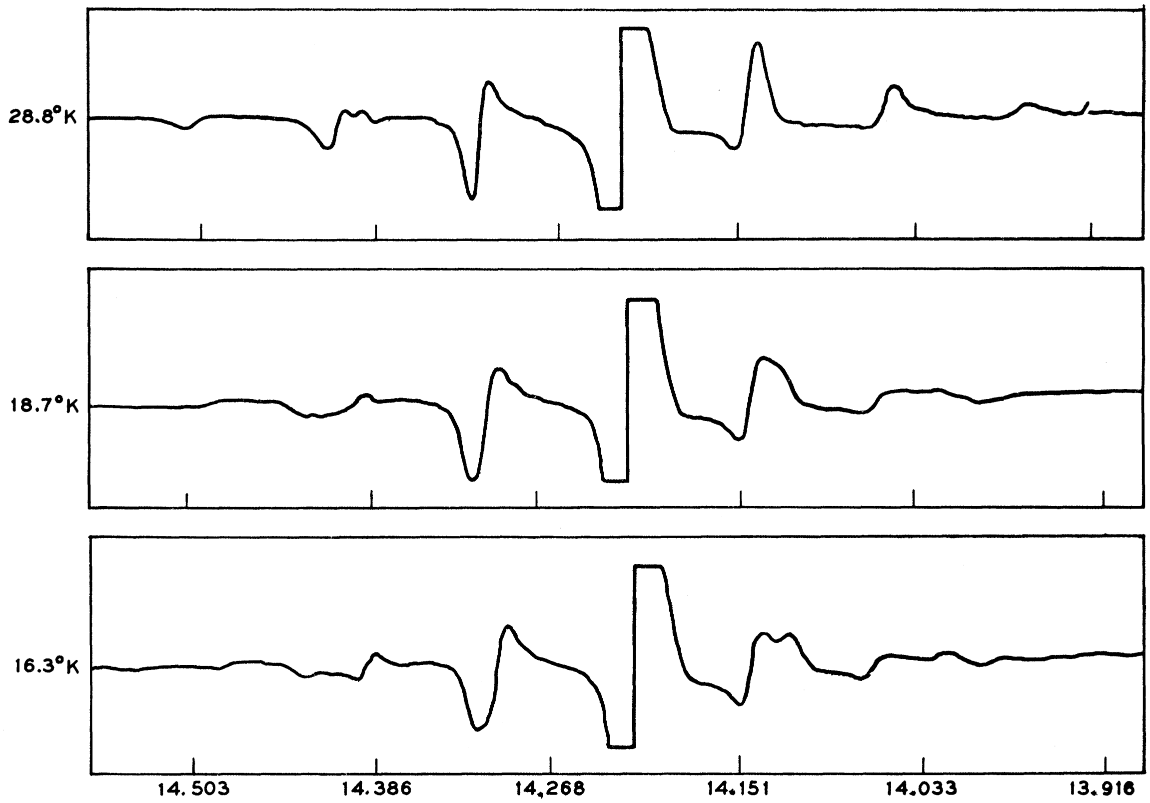

FIG. 1. Recorder traces of V^{51} nuclear-magnetic-resonance absorption derivative in V_3Si at 28.8, 18.7, and 16.3°K. The field decreases from left to right.

trical insulator, also allowed rf penetration. Heater power of less than 1 W, applied to the vial by a single turn of Nichrome wire, was sufficient to achieve any temperature from 20 to 77°K, provided some thermal isolation from the hydrogen bath was provided. The needed thermal isolation was obtained by immersing the vial and heater, which lie in the 1.1-cm inner diameter tip of a Dewar, in 400-mesh Al_2O_3 powder. By controlling the amount of powder on top of the sample, thermal time constants for equilibration between vial and bath temperatures from several seconds to several minutes were obtained. Temperatures were measured to the necessary accuracy with copper-constantan thermocouples. Measurements were made between 16 and 36°K. In the superconducting state below 16°K, sufficient flux exclusion occurred in these relatively coarse particles that the resonance signal was obscured by line broadening and noise.[7]

III. RESULTS

All of the nuclear resonance spectra observed show the splittings characteristic of nuclear electric quadrupole interactions (Fig. 1). Above 30°K, the observed patterns closely approximate those expected in a powdered sample when an axially symmetric electric field gradient (EFG) is present and when the nuclear magnetic energies are larger than the quadrupolar energies. The transition between nuclear Zeeman states m_I and m_I-1 should then occur to first order at a frequency of

$$\nu=\nu_0+(m_I-\tfrac{1}{2})\frac{3e^2qQ}{4I(2I-1)}(3\cos^2\theta-1)+\cdots,$$

where e^2qQ measures the magnitude of the interaction between the nuclear quadrupole moment Q and the axially symmetric electric field gradient q, where θ is the angle between the applied magnetic field H and the principal axis of the EFG tensor, and where ν_0 is the unshifted frequency. The crystal structure of V_3Si (Fig. 2) in its undistorted state is the $A15$ (β-wolfram) structure,[8] in which the vanadium point symmetry is $\bar{4}2m$. The V atoms lie in "chains" on the cube faces with nearest neighbors on the same face half a lattice constant up or down the chain. The chain forms the principal axis for the EFG. In experiments done on powders, all orientations of magnetic field with respect to the crystal axes occur. The intensity at the frequency corresponding to a given value of θ will, to first order

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[7] Observation of nuclear magnetic resonance in the superconducting state of V_3Si is possible in much more finely ground particles. A. M. Clogston, A. C. Gossard, V. Jaccarino, and Y. Yafet, Phys. Rev. Letters **9**, 262 (1962).

[8] H. J. Wallbaum, Z. Metallk. **31**, 362 (1939).

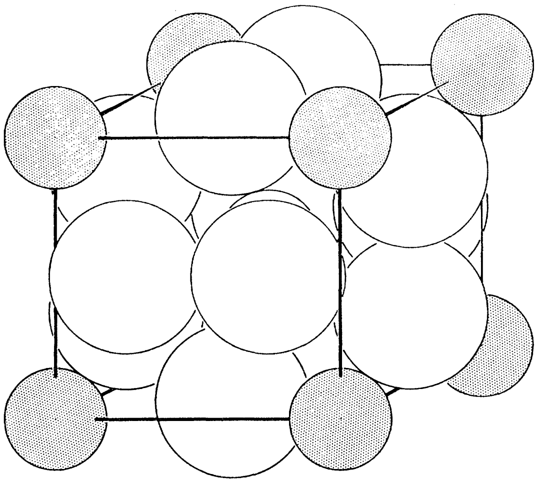

FIG. 2. $A15$ crystal structure of V_3Si in the undistorted state. Vanadium atoms lie on cube faces with nearest neighbors on the same faces at a distance $a/2$ along the V "chains." Silicon atoms lie at cube corners and centers.

in e^2qQ, be proportional to $(\cos\theta)^{-1}$ in the absence of other broadening mechanisms. Thus discontinuities occur at the frequencies corresponding to $\theta=\frac{1}{2}\pi$, and it is these discontinuities which are responsible for the three satellite peaks on either side of the $\frac{1}{2}\leftrightarrow-\frac{1}{2}$ transition in the higher temperature traces. The field difference between symmetrically spaced satellite lines on opposite sides of the central transition then gives the value of e^2qQ. Further, the center of gravity of each pair of satellites, when corrected for the second-order quadrupole shift, gives the field for resonance for just those nuclei with $\theta=\frac{1}{2}\pi$. Thus it measures the Knight shift for nuclei with magnetic field perpendicular to the symmetry axis. The central component on the other hand, includes contributions from nuclei with all values of θ and when corrected for its second-order quadrupole shift gives a weighted average of the Knight shift for all orientations of field. Thus a measurement of the respective centers of gravity can determine the anisotropy of the Knight shift. The 28.8°K value of e^2qQ and the values of Knight shift for $\theta=\frac{1}{2}\pi$ and for the weighted average of directions are given in Table I. Earlier work[9] has shown the Knight shift to be temperature-dependent, while the quadrupole interaction e^2qQ varies by less than 1% on warming to 300°K.

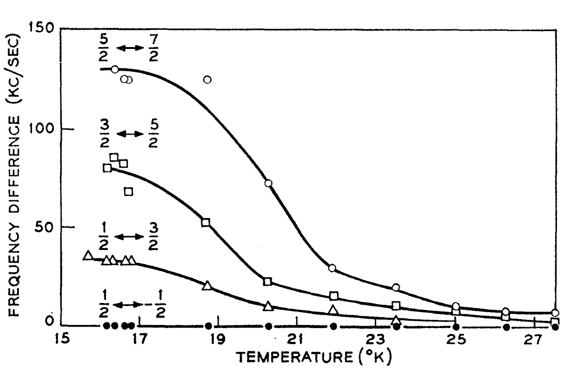

FIG. 3. Difference in frequencies of satellites from V^{51} nuclei on sites with increased field gradients and from V^{51} nuclei with decreased field gradients. The average of the splittings for the $m\leftrightarrow m-1$ and $-m\leftrightarrow-(m-1)$ satellites is given.

On cooling toward 16°K, a change in the spectrum developed. All of the satellites either broadened or split into doublets. Splittings of the low-field satellites were greater than of the high-field satellites, and the splittings were proportional to the distance from the central line. A plot of the observed splittings of the satellites as a function of temperature is shown in Fig. 3.

We have analyzed these results in terms of the development of two inequivalent sites, having distinct electric field gradients and fields for resonance. The NMR spectrum observed at 16.3°K could then be well approximated by taking two-thirds of the V atoms to lie on sites with the cubic (28.8°K) pattern with a reduced EFG and Knight shift, and one-third to lie on sites with the same pattern with an increased EFG and Knight shift. The best agreement could be obtained by assigning these component Knight shifts of 0.41% and 0.45%, respectively. The difference in Knight shifts accounts for the difference in splittings of low- and high-field satellites. Further improvement was obtained by including an untransformed component. The results for the best synthesis of a spectrum to match the observed 16.3°K spectrum are shown in Table I. Figure 4 shows the observed 16.3°K NMR pattern and the pattern which was synthesized using the parameters of Table I.

TABLE I. Electric quadrupole interaction e^2qQ and Knight shifts K of V^{51} nuclei in V_3Si. In the transformed state (16.3°K), two inequivalent sites develop. The a sites lie on (010) and (001) faces and have nearest neighbors in the $\pm x$ and $\pm y$ directions, respectively. The c sites lie on (100) faces and have nearest neighbors in the $\pm z$ directions. The Knight shift is anisotropic, with K(average) measuring a weighted average over all directions of magnetic field with respect to the crystal axes. $K(\theta=90°)$ measures the Knight shift for nuclei at sites with magnetic field perpendicular to the symmetry axis for the site.

		16.3°K	
Temperature	28.8°K	*a* sites	*c* sites
e^2qQ/h	2.924 Mc/sec ±0.015	2.674 Mc/sec ±0.015	3.262 Mc/sec ±0.015
$K(\theta=90°)$	0.39% ±0.01%	0.41% ±0.01%	0.45% ±0.01%
K(average)	0.45% ±0.01%	0.47% ±0.01%	

IV. DISCUSSION

The x-ray diffraction investigation of the structural transformation showed that the new low-temperature structure was tetragonal. A ratio of $c/a=1.0024$ was observed, although in many samples smaller distortions and incomplete transformations were observed.[5] This result is consistent with the NMR spectra since two inequivalent sites would be expected to develop in a tetragonal distortion leading to the development of two distinct electric field gradients and two fields for resonance. Vanadium atoms on chains running in the c direction would have nearest neighbors at a distance $c/2$ while V atoms on a and b chains would have neighbors at a distance $a/2$. The component of the resonance from the two sites with decreased EFG must arise from nuclei on sites with nearest neighbors lying in tetragonal a and b directions. The component from the one site with increased EFG then comes from the nuclei on sites with nearest neighbors in the tetragonal c direction. The unshifted component results from regions of incomplete transformation.

The fractional changes in electric field gradient found in the transformation were some two orders of magnitude greater than the changes in lattice constant in the transformation. The results of a calculation of the changes in EFG which would be produced by point charges on the atomic sites in a tetragonal distortion are given in Table II. The relative change due to this point-charge contribution is ~60 times smaller than the observed change and of opposite sign.

TABLE II. Comparison of calculated and observed field gradient behavior at V^{51} nuclei in V_3Si upon transformation. q_0 refers to the field gradient in untransformed (28.8°K) material, while q_a and q_c refer to the field gradients in the transformed (16.3°K) material at sites with nearest neighbors in the a and c directions. The calculated values are based on a point-charge approximation with equal charges at each of the two nearest V neighbors and at each of the four nearest Si neighbors.

	$\frac{q_a-q_0}{q_0}$	$\frac{q_c-q_0}{q_0}$
Calculated	+0.00144	−0.00192
Observed	−0.086	+0.116
Observed value/calculated value	−59.7	−60.5

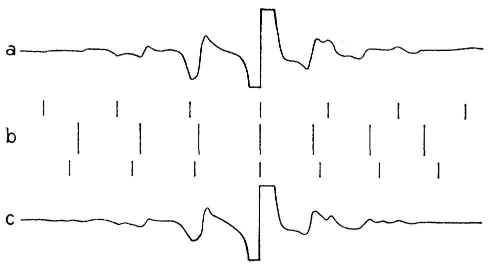

FIG. 4. (a) Observed resonance spectrum at 16.3°K. (b) Frequencies taken in synthesis of spectrum (see Table I). Half the atoms are taken to have reduced EFG, a quarter to have increased EFG, and a quater to be unchanged. (c) Synthesized resonance spectrum.

The uniqueness of this large change in EFG under the transformation becomes apparent when we compare the behavior of the electric field gradients observed in distortions in other systems. Ionic, covalent, and metallic systems have been observed under hydrostatic pressure.[10] For systems in which only the lattice parameter changes under pressure, one expects the EFG to vary as V^{-n}, with $n=1$ for a point-charge model. For gallium metal and the ionic salt Cu_2O, the point-charge-model prediction is obeyed. Covalent systems show a range of n about unity, with values as low as zero and as high as two. In V_3Si, on the other hand, the EFG varies by nearly 60 times the point-charge prediction, and evidently cannot be explained by either point charge or changing covalency effects. A more likely source of the V_3Si behavior involves the relatively high density of electrons near the Fermi energy in this material.

A consideration of the role of conduction electrons in electric field gradients of metals has shown that they play a dominant role in high density-of-states transition metals like V_3Si.[2] Since the total field gradient is a sum of point-charge, core, and conduction-electron contributions, it is possible for conduction-electron effects to outweigh point-charge and core effects. We believe that in V_3Si some of the characteristics of the Fermi surface electrons are changing by amounts of the order of 10% in the course of the transformation.

If the chains of vanadium atoms are treated as one-dimensional metallic lattices, then the change in EFG could be interpreted as reflecting different densities of states on the different chains. The c chains would thus have an increased density of states and the a chains a decreased one. Even if the chains are not strictly one-dimensional, we expect considerable anisotropy in the E-versus-k characteristics of electrons near the Fermi energy. Thus a band of electrons on the c chains of vanadium atoms might have the E-versus-k shown in Fig. 5 for directions of k along z, and along x or y. On expansion of the c axis during the transformation, the slope of E-versus-k_z would decrease and that of E-versus-k_x increase. A net increase in states with z-like

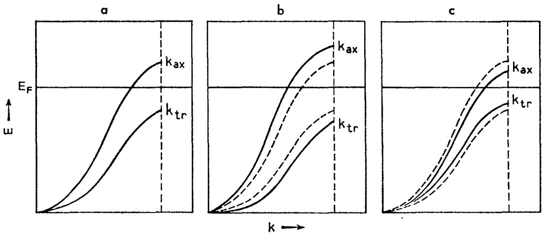

FIG. 5. Energy versus wave vector for wave vectors axial and transverse with respect to the principal axis of a vanadium chain. (a) Untransformed material. (b) Vanadium chains with decreased nearest-neighbor spacing. (c) Vanadium chains with increased nearest-neighbor spacing.

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[9] W. E. Blumberg, J. Eisinger, V. Jaccarino, and B. T. Matthias, Phys. Rev. Letters 5, 149 (1960).

[10] G. B. Benedek, *Magnetic Resonance at High Pressure* (Interscience Publishers, Inc., New York, 1963), p. 29.

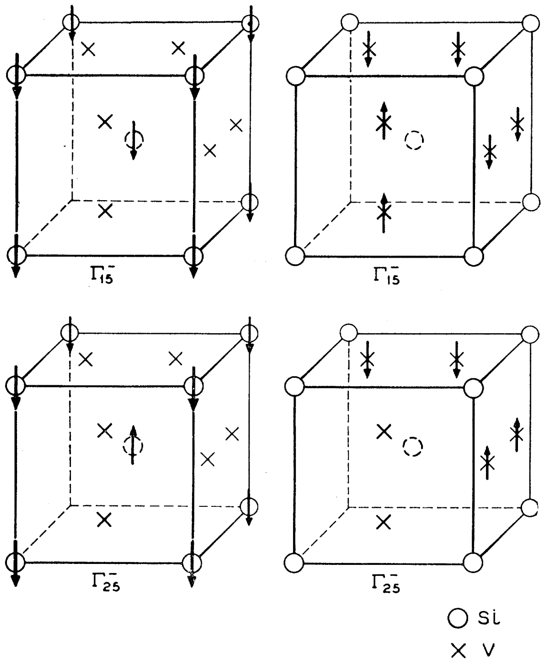

FIG. 6. Symmetry allowed distortions within the unit cell for a second-order phase transition.

symmetry would result,[11] leading to an increased conduction-electron field gradient as observed. The resulting decrease in the energy separation between states of z-like and x-like symmetry might also be expected to lead to an increased orbital paramagnetism on the c sites. This would lead to a more positive Knight shift on the c sites, again in agreement with the observed change in Knight shift. [*Note added in proof.* A model of the V_3Si transformation based on one-dimensional metallic lattices has been investigated recently by Labbe and Friedel (J. Labbe and J. Friedel, private communication, to be published). In their model, the Fermi energy of the undistorted V_3Si lies just above the zone boundary at the bottom of one subband of d electrons. On the chains which stretch, the d bands become narrower, with the bottom of the d subband in question passing above the Fermi energy. The net asymmetry in occupied d states, and hence the electric field gradient, is thus increased on the stretched chains. The electronic state density at the Fermi energy is substantially reduced, resulting in a smaller d-spin (more positive) Knight shift. On the chains which contract, the bottom of the widening d subband passes farther below the Fermi energy, resulting in more equal populations of the d subbands, a more symmetrical occupation of d states, a reduced electric field gradient, and a slightly reduced d-spin contribution to the Knight shift. These predicted effects all agree qualitatively with the observed behavior.]

In addition to the lattice constants a and c which change in the tetragonal distortion, it is possible that other parameters of the structure are changed in the transformation. The apparently continuous change of x-ray lattice constants and NMR field gradients as temperature is varied below the structural transition temperature implies that the transition is second order. But Blount and Anderson[12] have pointed out that a transition consisting solely of a tetragonal distortion would be expected to be first order, since a term in the energy of the crystal varying as the third power of the distortion exists. They argue that an additional distortion probably accompanies the development of tetragonality in V_3Si. It is of interest to see whether the nuclear magnetic resonance can provide any evidence for such additional distortions.

Blount has shown that the group-theoretical representations of the possible distortions from the V_3Si crystal structure are Γ_{15}^-, Γ_{25}^-, Γ_{12}^+, Γ_{15}^+, Γ_2^+, and Γ_{25}^+, where the plus and minus signs refer to the parity of the representations.[13] Since the distortions are required to have tetragonal symmetry, the representations Γ_2^+ and Γ_{25}^+ may be eliminated. The Γ_{12}^+ and Γ_{15}^+ distortions may also be eliminated, since for these representations, $\Gamma_i \times \Gamma_i \times \Gamma_i$ contains Γ_1^+. A third-order invariant thus exists, and from the Landau theory of phase transitions,[14] these representations correspond to first-order transitions. Only the Γ_{15}^- and Γ_{25}^- distortions remain and satisfy the tetragonality and the second-order transition requirements. The atomic displacements corresponding to these distortions are shown in Fig. 6. Two consist of motion of V sites and two of motion of Si sites. We have calculated the change in field gradient at the V sites from point charges at the first- and second-nearest-neighbor sites for each of these distortions. Only for the Γ_{25}^- distortion of the Si [Fig. 6(c)] is there a change in field gradient. For this distortion, a total of three distinct field-gradient values, one from a sites and two from c sites are expected. In the experimental NMR spectra, however, we can neither resolve nor find evidence for the existence of three field gradients. Thus NMR provides no evidence for this Γ_{25}^- Si distortion. The remaining allowed distortions (as well as the first-order Γ_{12}^+ and Γ_{15}^+ distortions) were found to give no change in the point-charge field gradients to first order. Thus NMR would not be expected to provide a sensitive test for these distortions, and their presence might be undetected.

V. CONCLUSION

The low-temperature structural transformation of V_3Si is reflected in the NMR spectrum of the V^{51} nuclei.

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[11] It is assumed that states with wave vectors in the z direction have a z-like charge distribution.

[12] P. W. Anderson and E. I. Blount, Phys. Rev. Letters **14**, 217 (1965).

[13] E. I. Blount (private communication).

[14] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958), p. 439.

The NMR spectrum is obtained from polycrystalline material and presents a means of detecting such transformations in cases where single crystals are not available. We have been able to determine that no comparable distortion occurs in V$_3$Ga.

The unexpectedly large changes in electric field gradient which occurred in the transformation indicate that effects of uniaxial stress could be observed in the NMR of single crystals of the vanadium β-tungsten-structure compounds. Such measurements would be useful in establishing a firmer correlation between the density of conduction-electron states at the Fermi energy and the electric field gradients in metals.

The changes in EFG found in the present work are of a magnitude which demonstrates that conduction electrons contribute dominantly to the vanadium quadrupole interaction in V$_3$Si and that a significant change in electronic band structure occurs in the transformation. The changes found in the Knight shift also reflect the change in the electronic band structure.

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Dynamic Effects in Paramagnetic Resonance of Magnetic Ions in Metals[*]

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The transverse susceptibility, which determines the paramagnetic resonance behavior, is studied for paramagnetic ions coupled by an effective scalar exchange interaction to the conduction electrons of a host metal. By means of a temperature Green's-function technique for ionic spins, it is found that the dynamical behavior of the conduction electrons influences the ionic resonance if the relaxation rate of the conduction electrons is not large compared to their resonance frequency. The predicted effects, namely, a broadening at low temperature, a shift around the Curie temperature, and a diminished broadening at high temperature, are compared with experimental data. The last effect can also be seen in nuclear resonance, whereas, the other effects appear only in ionic resonance experiments, since only the ionic Zeeman energy is comparable with the Zeeman energy of the conduction electrons. The theory suggests a possibility for distinguishing between direct and indirect exchange coupling of ions in metallic solutions, since in the first case the resonance signals are exchange-narrowed, whereas, in the second case they are broadened by a dissipative contribution of the conduction electrons.

1. INTRODUCTION

THE magnetic resonance of paramagnetic ions in metals has been studied by several authors.[1–3] It is well known that the resonance frequency in these experiments is given by[2]

$$\omega_H=\omega_i+\bar{J}\chi_z^{\mathrm{el}}(H_z/\mu N)\equiv\omega_i+\delta\omega\,, \tag{1.1}$$

where χ_z^{el} is the static paramagnetic susceptibility of the conduction electrons, $\bar{J}$ is the effective exchange parameter[4] between ions and conduction electrons, H_z is the applied static field, ω_i is the resonance frequency of the free ions, μ is the Bohr magneton, and N is the number of lattice points per unit volume. We wish to point out here that this relation holds only in the limits where $\omega_i \ll \omega_{\mathrm{el}}$, or where the relaxation rate of the conduction electrons $\Delta \gg \omega_{\mathrm{el}}$ (ω_{el} is the resonance frequency of the conduction electrons), or finally where $kT \gg \hbar\omega_i$.

If none of these conditions are fulfilled, then the dynamical effects of the conduction electrons become important and the g shift and broadening in ionic resonance experiments are no longer analogous to the Knight shift and Korringa broadening known from nuclear resonance. Some anomalous observations on

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[*] This work was partially supported by the Swiss National Science foundation.

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