CORRELATIONS BETWEEN SUPERCONDUCTIVITY AND NUCLEAR MAGNETIC RESONANCE PROPERTIES

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(Received July 27, 1960)

Using nuclear magnetic resonance (NMR) techniques, we have measured the Knight shifts,[1] linewidths, and quadrupole interactions in a series of vanadium intermetallic compounds V_3X (where X = As, Au, Co, Ga, Ge, Ir, Pt, Sb, Si),[2] all having the β-wolfram structure.[3] These experiments reveal certain striking correlations between the NMR properties and the superconducting transition temperatures of these compounds. Measurements were made with a Varian NMR spectrometer in a temperature range between 4°K and 400°K using 400-mesh particles.

Vanadium Knight shifts k_V, which were measured relative to KVO_3 solution, are shown as functions of temperature in the upper part of Fig. 1. While Knight shifts normally are expected to be temperature independent, several of these V_3X compounds show a marked temperature dependence of k_V. This temperature dependence is several orders of magnitude greater than and in the opposite direction from that expected from lattice contraction. The compounds with the highest superconducting transition temperature T_c, shown at the right of Fig. 1, have k_V's with the greatest variation with temperature, while compounds which are not superconductors or have low transition temperatures have temperature-independent Knight shifts. Pure V metal is included in Fig. 1 for comparison.

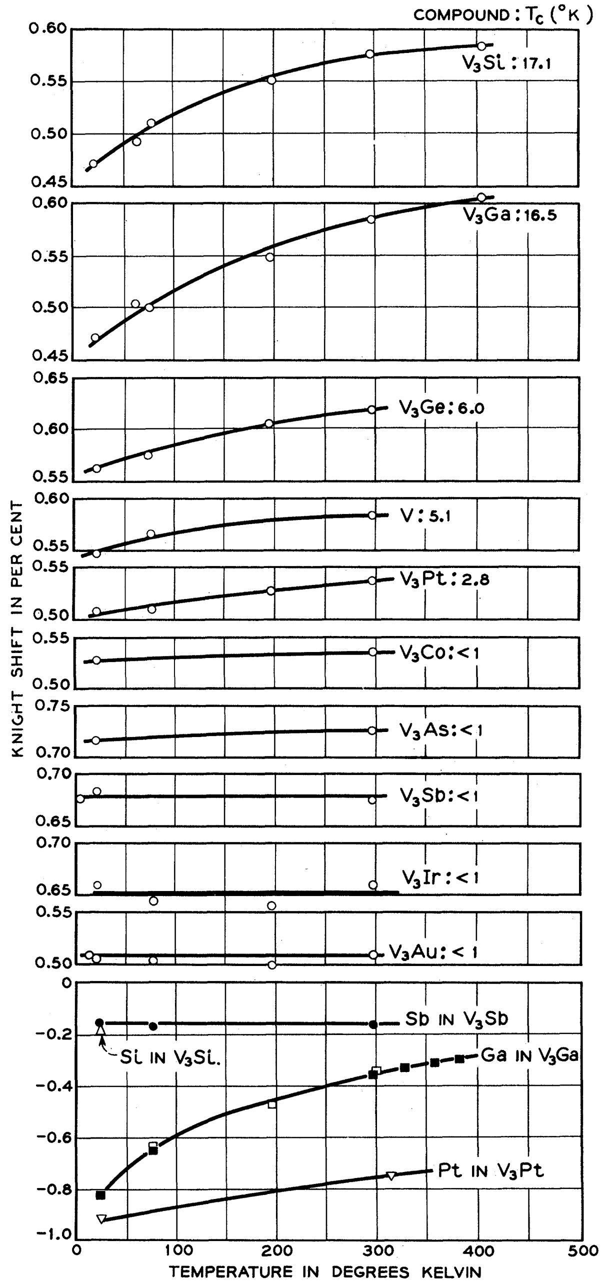

FIG. 1. Knight shifts k_V and k_X in % vs temperature for the intermetallic compounds V_3X. The values of k_V appear in the upper portion of the figure and are all positive; the k_X appear in the lower portion and are all negative. (k_{Co} is an exception to this rule and is discussed in the text.) Note that the scales for k_V and k_X are different. The superconducting transition temperatures T_c are tabulated at the right.

The Knight shifts of the minority constituents of these compounds are shown in the lower part of Fig. 1. Some previous measurements[4] on V_3Ga are shown by the open squares. While the NMR of the minority constituents of only a few compounds can be studied, all of these show <u>negative</u> Knight shifts (i.e., diamagnetic shifts) with the exception of V_3Co which shows a temperature-independent $k_{Co} = +0.7\%$. Note that k_{Ga} in V_3Ga exhibits a strong temperature dependence.

The V-Ga intermetallic system forms the β-W structure in a wide range of composition (the V/Ga ratio is variable between the limits of 2 and 4). In the case V/Ga $\neq$ 3, the excess V or Ga occupies Ga or V positions, respectively. The composition V/Ga = 3 is analogous to a pure metal, while the case V/Ga $\neq$ 3 is somewhat analogous to a substitutional alloy and may be termed a mixed intermetallic compound. In this range the superconducting transition temperature[5] T_c has a maximum of 16.5°K at V/Ga = 3, decreasing monotonically on the Ga-rich side to 7.6°K at V/Ga = 2 and on the V-rich side to 10.1°K at V/Ga = 4. Figure 2 shows k_V and k_{Ga} for this system plotted as functions of T_c, with the temperature at which measurements were made as a parameter. Note that the compounds with the highest T_c show the greatest temperature dependence in both k_V and k_{Ga} (see Fig. 1).

The linewidths δH of the vanadium resonances measured between absorption derivative extrema are shown as a function of temperature in Fig. 3. At room temperature all V linewidths shown were approximately equal to that of V metal. The δH for all these compounds was independent of the magnetic field and essentially independent of temperature except in the case of V_3Ga. In addition, the V linewidth was found to be 15 oe in V_3Au and 50 oe in V_3Sb at 300°K and 14 koe. These linewidths, however, decreased at lower fields, showing that some anisotropic magnetic interaction not important for the other compounds determines δH for V_3Au and V_3Sb. The Ga^{71} linewidth in V_3Ga increased from 9 oe at 295°K to 40 oe at 20°K, while δH for Pt and Sb remained constant.

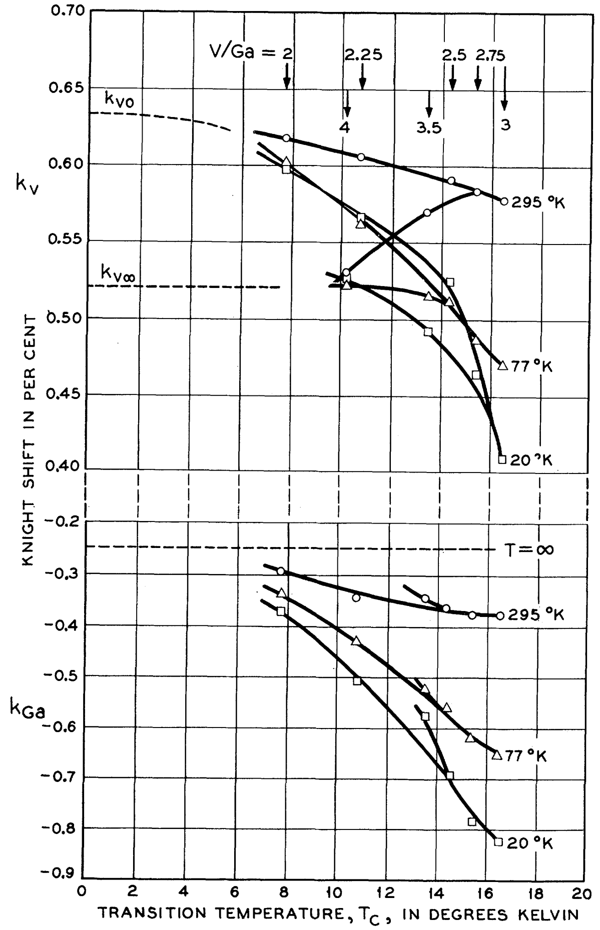

FIG. 2. Knight shift k vs T_C for the mixed intermetallic compound system V-Ga with the β-W structure. The value for k_V and k_{Ga} appear in the upper and lower portions of the figure, respectively. Note that the ordinate scales are different and that $k_V > 0$ while $k_{Ga} < 0$. The T_C corresponding to a given V/Ga ratio is given at the top. The extrapolated limits k_{V0} and $k_{V\infty}$ corresponding to V/Ga = 0 and ∞, respectively, refer to the expected local susceptibility difference between solvent and solute atoms as computed by J. Friedel, Phil. Mag. 43, 153 (1952). The extrapolated value for k_{Ga} at $T = \infty$ indicates that in the β-W structure it is intrinsically negative.

Most of the V resonance lines showed some quadrupole splitting.[6] The symmetry of the V site allows an axial electric field gradient. In Fig. 4 we have plotted e^2qQ against T_c of the compound involved. We note that there is a general trend for the superconductors having higher T_c to also have larger e^2qQ.

It is interesting to note that the magnitude of k_V for all these compounds except V_3As and V_3Sb is within 7% of k_V for V at room temperature. The fact that the temperature dependence of k_V in the case of V_3Si and V_3Ga is five times larger than the variation between the various compounds suggests that the temperature dependence of k_V be associated with the superconducting properties rather than with the particular kind of atom occupying the minority site. In the V-Ga system it

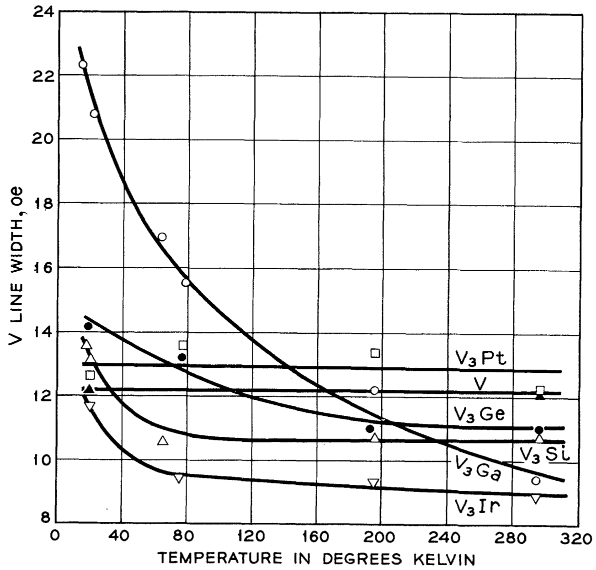

FIG. 3. Linewidth of V resonance as a function of temperature.

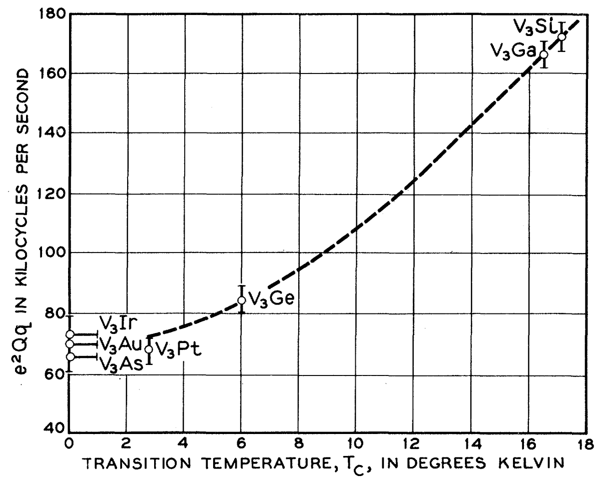

FIG. 4. Quadrupole interactions of V in β-W intermetallic compounds vs superconducting transition temperature. For V in V_3Co an anomalously large e^2qQ of 1.0 Mc/sec is observed (see discussion in the text).

is clear that the temperature dependence of k_V and k_{Ga} does not arise directly from the change in composition but is a function of the superconducting transition temperature. That is to say, those interactions which are responsible for the magnitude of T_c are also responsible for the temperature dependence of k.

At room temperature, linewidths of the V resonances are all considerably larger than the direct nuclear dipole-dipole interaction would allow. The two high-temperature superconductors show distinctly different temperature dependence: the V linewidth in V_3Ga suffers a large increase at low temperatures while that in V_3Si does not. We believe that the temperature-dependent and temperature-independent parts of δH arise, respectively, from the isotropic and anisotropic parts of the indirect nuclear exchange interaction[7] via the conduction electrons. Line broadening arises from the isotropic part only for dissimilar moments, but the anisotropic part produces broadening from the interaction between all moments. (All Ga nuclei have relatively large magnetic moments while less than 5% of the Si nuclei have any moment at all). The behavior of the Ga and Si resonances in these compounds is also consistent with this interpretation. However, δH for none of the low-temperature superconductors or nonsuperconductors has an appreciable temperature dependence, regardless of the abundance and size of the nuclear moments at the minority site. Those electrons which are directly responsible for the Knight shift and the isotropic indirect exchange interaction are the s electrons. The absence of the temperature dependence of δH in that case where isotropic indirect exchange is not possible suggests that we associate the temperature-dependent effects in the superconductors with the s electrons.

In the absence of extraordinary shielding by conduction electrons, one would expect from the behavior of the noncubic pure metals that the quadrupole interaction at the V site would be several Mc/sec. The smallness of e^2qQ is thus puzzling, but perhaps the most surprising feature is that the magnitude of e^2qQ should increase with increasing T_c. Thus, it appears that those interactions which are responsible for the magnitude of T_c decrease the shielding of the quadrupole interaction at the V site.

The facts that all the k_V are approximately the same and that all V atoms have only other V atoms as nearest neighbors, suggest a model for these compounds in which the V atoms form a sublattice having electronic properties not unlike V metal. The atoms at the minority site have only V neighbors and thus do not form such a sublattice. The fact that the Knight shifts are negative at the X sites in V_3X, whereas they are positive in each pure X metal, suggests that due to the formation of the intermetallic bond, the polarization of the available outer s electrons is reversed. This is in contrast to isolated solute metal atoms in a solvent metal lattice where the observed k_{solute} is always positive. The positive k_{Co} in V_3Co indicates that perhaps V_3Co is more like the latter "alloy" case than the former "intermetallic compound" case in that the overlap of the like s- and d-band electrons of Co and V negate the bonding effects, although V_3Co in all its other physical properties behaves like an intermetallic compound. It is interesting to note in this respect that V_3Co has an anomalously large V quadrupole interaction relative to the other V_3X compounds.

To our knowledge this is the first time that correlations have been observed between T_c and local atomic properties. These correlations exist at temperatures well above the superconducting region.

We wish to thank E. Corenzwit for making many of the compounds studied in these experiments, Mrs. V. Compton for x-ray analysis verifying their β-wolfram structure, and A. M. Clogston and H. Suhl for many instructive discussions.

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[1] C. H. Townes, C. Herring, and W. D. Knight, Phys.

Rev. 77, 852, (1950), W. D. Knight, in Solid-State Physics, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1956), Vol. 2, p. 93.

[2] In addition to these compounds, V_3Sn was also prepared, but it was not possible to make it without excess metal dispersed in the lattice, although this was possible for all other samples. The samples were prepared by direct combination of the metals in an arc furnace.

[3] S. Geller, Acta Cryst. 9, 885 (1956). The β-wolfram structure has space group $Pm\bar{3}n$. The point group at the V site is $\bar{4}2m$ and at the X site $m3$.

[4] R. G. Shulman, B. J. Wyluda, and B. T. Matthias, Phys. Rev. Letters 1, 278 (1958).

[5] T_C for these mixed intermetallic compounds is reported here for the first time.

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[7] M. A. Ruderman and C. Kittel, Phys. Rev. 96, 99 (1954).

MÖSSBAUER EFFECT IN Fe^{57} AT VERY LOW TEMPERATURES

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(Received July 14, 1960)

The recoil-free gamma-ray transition between the 14.4-kev state and the ground state of Fe^{57} has been used to study the hyperfine splittings of these levels in several crystals.[1-4] The studies of the magnetic hyperfine spectra in metallic iron[1] have shown the gamma ray to be split into six components characterized by a ground-state level separation $g_0 = 1.90 \times 10^{-7}$ ev, and a first excited state splitting of 1.07×10^{-7} ev. The separation of the ground-state levels is equivalent to a temperature of 2.2×10^{-3} °K, which has suggested to us the possibility of observing the effects on the Mössbauer fluorescence pattern that can be produced by cooling a resonant absorber to very low temperatures. In thermal equilibrium the population ratio of the Zeeman levels of the ground state of absorbing Fe^{57} nuclei ($I = 1/2$) varies with temperature as $\exp(-g_0/kT)$. Such a population asymmetry would produce an increased absorption coefficient for a transition arising from the $m = -1/2$ Zeeman level relative to transitions in which the m value is reversed in sign. Examination of these absorption coefficients could be made by measuring the transmission of resonant gamma rays from a source at room temperature, by the technique of Doppler-shifting the source relative to the cold absorber.

Larger asymmetries are produced by cooling the source instead of the absorber, since the Co^{57} parent has a magnetic moment about 50 times larger than that of the ground state of Fe^{57}. Success of this scheme depends upon the reasonable expectation that the decay of the Co^{57} through the second and first excited states of Fe^{57} proceeds so rapidly that the Zeeman level populations are unchanged.[5] The process is complicated and the over-all effect reduced, however, by the partial mixing of levels according to the character of the decay. Calculations based upon the assumptions that the electron capture process of Co^{57} is an allowed transition and that the decay from the second to the first excited state of Fe^{57} is either $M1$ or $E2$[6] indicated a partial preservation of the Co^{57} population ratios. These calculations predicted a larger over-all effect than the simpler scheme of cooling an absorber; accordingly the experiment was performed with a cold source and an absorber at room temperature.

A source of approximately 10 millicuries of Co^{57} in natural Fe metal was prepared by the usual technique of plating followed by thermal diffusion,[7] and installed in an adiabatic demagnetization cryostat fitted with thin windows of Mylar plastic and Be metal. The source foil was soldered to the bottom of a capsule containing about 0.1 mole of chromium potassium alum crystals in toluene, and this capsule was thermally attached to a liquid He^3 reservoir by a Pb "heat switch". The 14.4-kev radiation was filtered by a resonant absorber of approximately 2 mg/cm² Fe^{57} plated on 0.1 mil nickel foil. The absorber was situated outside the cryostat in a frame which could be oscillated linearly at various speeds by means of a synchronous motor, gear train, and cable system. Transmitted intensities were measured using a 1-mm thick NaI(Tl) crystal and photomultiplier, single-channel pulse-height analyzer, and digital printer. Periods of oscillation were varied from 3 seconds to 5 minutes, and intensities were measured alternately in each direction over the same length of absorber travel. Special care was exercised