Nuclear magnetic resonance of V^{51} in a V_3Si single crystal

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An investigation was made of the nuclear magnetic resonance of V^{51} in a V_3Si Single crystal at the boiling point of liquid nitrogen. It was established that the tensor of the electric field gradient at the sites of the vanadium nuclei was axially symmetric and its symmetry axis coincided with the directions of the chains of the transition element atoms, i.e., with the [100] directions. The quadrupole splitting parameter, the isotropic and anisotropic Knight shifts were, respectively $\nu_Q=0.205\pm0.001$ MHz, $K_{is}=0.43\pm0.02\%$, and $K_{an}=0.04\pm0.015\%$.

The present paper describes an investigation of the nuclear magnetic resonance (NMR) of V^{51} in a single crystal of V_3Si, which is an intermetallic compound distinguished by the highest superconducting transition temperature among vanadium compounds.

Vanadium silicide has the A-15 crystal structure. The atoms of the transition element occupy sites in a bcc lattice, whereas the silicon atoms are distributed in pairs on the faces of a unit cell, forming three families of nonintersecting chains. The quasi-one-dimensional nature of the distribution of the transition element atoms has been used in calculations of the Fermi surfaces[1] and band structures of V_3X compounds,[2,3] which have explained the anomalous properties of these intermetallic compounds exhibited in the temperature dependence of the paramagnetic susceptibility, elastic properties, and Knight shifts of the nuclei of the transition and nontransition elements.

The data obtained from the NMR measurements provide a basis for the calculation of the densities of various electron states on the Fermi surface and for estimates of the contribution of the orbital magnetism to the magnetic susceptibility and hyperfine fields at the nuclei. Hence, it is desirable to know the exact values of the Knight shift and other NMR parameters. The most reliable values of all the NMR parameters, including the orientation of the principal axes of the tensor of the electric field gradient at the sites of the investigated nuclei, are obtained for single crystals.

In the present study we established that the tensor of the electric field gradient has the axial symmetry: the symmetry axis is aligned along the [100] crystallographic direction. We obtained the values of the isotropic and anisotropic components of the Knight shift and of the quadrupole splitting ν_Q.

A single crystal of V_3Si was grown by the floating zone method using an induction heater[4] in an atmosphere of spectroscopically pure argon (2 atm). The initial components were an outgassed vanadium of the VÉL-1 grade and undoped silicon of the semiconductor grade. A blank of 10 mm diameter was prepared by fusing together 25.5 at.% silicon and 74.5 at.% vanadium. The first zone melting was carried out in vacuum (5×10^{-6} mm Hg) at a rate of 5 mm/min. Argon was then admitted into the vacuum chamber and a crystal was grown from a seed at a rate of 0.2 mm/min. A sample obtained in this way was subjected to a homogenizing annealing in an argon atmosphere at 1600° applied for 30 h. This was followed by electrolytic polishing in a 10% solution of NaOH which removed a surface layer 1 mm thick.

Chemical, metallographic, and x-ray diffraction analyses demonstrated that the crystal obtained was homogeneous and of stoichiometric composition. The lattice period was 4.724 ± 0.001 Å. The superconducting transition temperature, measured by an induction method, was 16.6°K and the width of this transition was 0.3 deg K. This was also evidence of homogeneity of the composition and its stoichiometry. Moreover, the high quality of our single crystal was supported by the resistance ratio R(300°K)/R(20°K) = 12. At 78°K the resistivity was ρ = 20 $\mu\Omega$.cm.

A single-crystal rod of 7 mm in diameter and 15 mm in length was used to prepare a "comb" of plates 0.2 mm thick. This thickness was comparable with the skin depth in the range of radio frequencies employed in our study. The planes of the plates in the "comb" were aligned along the (100) planes and the [100] axis coincided with the axis of the cylinder.

A sample was placed in a coil supplied from a high-frequency small-signal oscillator,[5] placed in a Dewar flask kept at liquid nitrogen temperature. A polarizing magnetic field of 3.9 kOe was modulated at 412 Hz and the modulation amplitude was 3 Oe. The magnetic field was determined accurately using the Cu^{63} resonance.

Figure 1 shows the orientation of a sample in our measurements. The [001] crystallographic direction of the sample was perpendicular and the [100] direction was parallel to the external magnetic field. The resonance absorption spectra were recorded in the course of rotation of the single crystal about the [001] axis in steps of 5° (from $\varphi_1 = 0$ to $\varphi_1 = 90°$). The angle between the external magnetic field and the [001] direction and the angle in the rotation were set to within 2°.

The presence of electric field gradients in compounds such as vanadium silicide is attributed in[6] to the anisotropy of the electron density in quasi-one-dimensional chains of the transition element atoms. If we assume that a crystal contains three mutually perpendicular systems of such chains, we find that the NMR spectrum should represent the sum of three spectra typical of uniaxial crystals.[7] These spectra should differ in the nature of changes in the satellite structure with the orientation of the crystal relative to the external magnetic field.

Let us consider the expected change in the NMR spectrum on the assumption that the tensor of the electric field gradient and the Knight shift are axially symmetric.

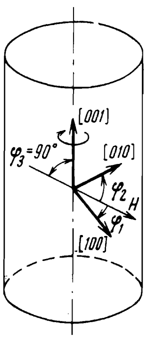

FIG. 1. Position of a sample relative to the applied magnetic field.

We shall show later that this assumption is fully justified. Jones, Graham, and Barnes[8] obtained the following relationship for the NMR frequency of uniaxial crystals:

$$\nu(m\leftrightarrow m-1)=\nu_0'(1+K_{\text{is}})\left\{1+(3\mu^2-1)\left[a+\frac{\nu_Q}{2\nu_0}\left(m-\frac{1}{2}\right)\right]\right.$$
$$+\frac{\nu_Q{}^2}{32\nu_0{}^2}(1-\mu^2)\left\{[102m(m-1)-18I(I+1)+39]\mu^2-[6m(m-1)\right. \quad (1)$$
$$\left.\left.-2I(I+1)+3]\right\}+\frac{\nu_Q{}^3}{3\nu_0{}^3}(2m-1)(1-\mu^2)P_3(m,\mu)\right\},$$

where $\nu_Q = 3e^2qQ/2I(2I-1)h$; $a = K_{\text{an}}/(1+K_{\text{is}})$; $\mu = \cos\theta$; θ is the angle between the external magnetic field and the symmetry axis of the tensor of the electric field gradients; ν_0' is the resonance frequency in the absence of the quadrupole effects and Knight shift; m is the quantum magnetic number; K_{is} and K_{an} are the isotropic and anisotropic components of the Knight shift; e is the electron charge; Q is the quadrupole moment of the investigated nuclei; q is the gradient of the electric field at the sites of the investigated nuclei; I is the spin of the investigated nuclei; h is the Planck constant; $P_3(m, \mu)$ is a function for which an analytic expression is given in[7].

It is clear from this relationship that if in the absence of the quadrupole interaction ($\nu_Q = 0$) the NMR spectrum consists of a single line whose frequency depends on the parameter μ, the quadrupole interaction lifts the degeneracy in respect of the quantum magnetic number m and the single resonance line splits into 2I components, in accordance with the selection rule $\Delta m = \pm 1$. The frequency of each resonance ν ($m \rightleftarrows m-1$) depends on the orientation of the symmetry axis of the tensor of the electric field gradient and of the Knight shift relative to the external magnetic field, i.e., it depends on the parameter μ.

In the adopted method the angle φ_3 remains constant during the rotation of the single crystal and, consequently, if the tensor of the electric field gradient is axially symmetric and the symmetry axis is parallel to the [001] chains, the nuclei belonging to these chains (Fig. 1) give rise to six satellite resonances at fixed frequencies. The lack of dependence of the resonance frequencies on the azimuthal angle is a direct proof of the axial symmetry of the tensor of the electric field gradient and of the alignment of its symmetry axis along the axis of rotation.

The changes in the satellite structures of the NMR spectra of the nuclei in the [100] and [010] chains as a result of rotation, which increases the angle φ_1 from 0 to 90°, can be obtained from Eq. (1) for $\theta = 0$–$90°$ for the [100] chains and $\theta = 90$–$0°$ for the [010] chains.

The angular dependences of the resonance frequencies of the satellite transitions, obtained by analysis of the NMR spectra of V^{51} in a V_3Si single crystal, are plotted in Fig. 2. The frequencies of the central components of the resonance spectra are not given because their shifts resulting from the change in μ may reach about 25 kHz due to second-order quadrupole effects. Since the widths of the individual resonance lines are 10 kHz, the resolution is poor.

It is clear from Fig. 2 that the structure of the spectra is of the expected type. In full agreement with the theory and geometry of the experiment, there are six satellite resonances whose frequencies remain constant (within the limits of the experimental error) during rotation of the single crystal. These resonances should be attributed to the chains of nuclei of the [001] type (Fig. 1). It follows that the tensor of the electric field gradient and the Knight shift are axially symmetric and that their symmetry axes are parallel to one another and to the axis about which the single crystal is rotated. Consequently, Eq. (1) can be used in the analysis of the obtained spectra. The remaining 12 satellite resonances can readily be interpreted as the satellite structures of the resonances of the nuclei in the [100] and [010] chains: this follows from the nature of the dependences of the resonance frequencies on the angle of rotation of the single crystal relative to the external magnetic field. Thus, the symmetry axis of the tensor of the electric field gradient at the sites of the vanadium nuclei is directed along the chain of atoms in which the resonating nuclei are located.

In the case of the axially symmetric tensor of the electric field gradient and Knight shift, the NMR can be described fully by three parameters: the quadrupole splitting parameter ν_Q and the isotropic and anisotropic components of the Knight shift (K_{is} and K_{an}). We shall calculate these parameters from the curves plotted in Fig. 2.

In order to find ν_Q we shall consider pairs of satellites for $\varphi_1 = 0$ [in Eq. (1) this corresponds to $\theta = 0°$] with the following quantum numbers: $7/2 \rightleftarrows 5/2$; $-5/2 \rightleftarrows -7/2$ and $5/2 \rightleftarrows 3/2$; $-3/2 \rightleftarrows -5/2$. Using Eq. (1), we can easily show that the separations between the satellites in these pairs should be $6\nu_Q$ and $4\nu_Q$, respectively. Taking these separations from the experimental data, we find that $\nu_Q = 0.205$ MHz. For this angle φ_1 the satellite resonances are not superimposed and, therefore, we can measure the resonance frequencies to within ± 1 kHz. Thus, $\nu_Q = 0.205 \pm 0.001$ MHz. A calculation based on the quadrupole coupling constant obtained in[6] for V_3Si at 28°K gives $\nu_Q = 0.209 \pm 0.001$ MHz. The difference of 4 kHz between these values may be due to the influence of the dipole-dipole width of the resonance line, which must be included in the determination of the quadrupole interaction parameter from the

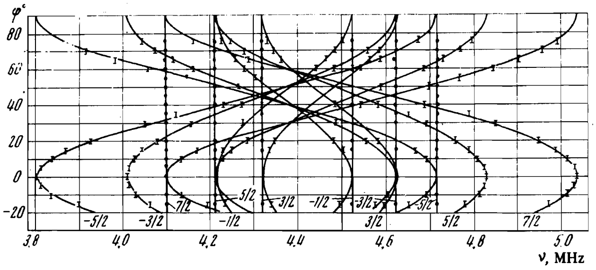

FIG. 2. Experimental values of the resonance frequencies of the V^{51} satellite NMR transitions in a single crystal of V_3Si oriented in different ways relative to the applied magnetic field (T = 78°K).

NMR spectra of polycrystalline samples. This parameter carries information on the electric field gradient at the sites of the vanadium nuclei. The value of the gradient can be deduced from the exact value of the quadrupole moment of the V^{51} nuclei.

We shall determine the anistropic component of the Knight shift using the fact that the expression for the average frequency of any satellite pair includes the parameter $a = K_{an}/(1 + K_{is})$. In fact, for the satellite pairs considered above at $\theta = 0°$, we obtain

$$\begin{gathered}\nu(^7/_2 \leftrightarrow {}^5/_2) + \nu(-^5/_2 \leftrightarrow -^7/_2) = 2\nu_0(1+2a),\\ \nu(^5/_2 \leftrightarrow {}^3/_2) + \nu(-^3/_2 \leftrightarrow -^5/_2) = 2\nu_0(1+2a),\end{gathered} \tag{2}$$

where $\nu_0 = \nu_0'(1 + K_{is})$. If these frequencies are deduced from the experimental results, we find that

$$\nu_0 + 2a\nu_0 = 4.420 \text{ MHz}. \tag{3}$$

For the same satellite pairs at $\theta = 90°$ the average values of the frequencies are, respectively,

$$\begin{gathered}{}^1/_2[\nu(^7/_2 \leftrightarrow {}^5/_2) + \nu(-^5/_2 \leftrightarrow -^7/_2)] = \nu_0(1-a) - 3\nu_Q^2/4\nu_0 = 4.4076 \text{ MHz},\\ {}^1/_2[\nu(^5/_2 \leftrightarrow {}^3/_2) + \nu(-^3/_2 \leftrightarrow -^5/_2)] = \nu_0(1-a) + 3\nu_Q^2/16\nu_0 = 4.4139 \text{ MHz}:\end{gathered} \tag{4}$$

The numerical values of the frequencies are found by averaging the experimental values over all the recorded spectra. If we include corrections due to the second-order quadrupole effects, assume that $\nu_Q = 0.205$ MHz and $\nu_0 = 4.418$ MHz, and average over two pairs of satellites, we obtain

$$\nu_0 - a\nu_0 = 4.4133 \text{ MHz}. \tag{5}$$

Solving Eqs. (3) and (5) simultaneously for a and ν_0, we find that $a = 4.3 \times 10^{-4}$ and $v_0 = 4.416$ MHz.

The standard resonance frequency of the Cu^{63} nuclei in the magnetic field employed is 4.444 MHz and hence we can easily obtain the resonance frequency of the V^{51} nuclei with zero Knight shift: $\nu_0' = 4.3973$ MHz. Comparing ν_0 and ν_0', we obtain the isotropic component of the Knifht shift $K_{is} = 0.43 \pm 0.02\%$, Since $a = K_{an}/(1 + K_{is})$, the anisotropic component of the Knight shift is $K_{an} = 0.04 \pm 0.015\%$.

If we use these NMR parameters and Eq. (1), we can calculate the dependences of the resonance frequencies of the satellites on the angle θ. These dependences are represented by the continuous curves in Fig. 2. It is clear that the experimental values are in agreement (within the limits of the error) with the calculated curves.

Thus, measurements on a V_3Si single crystal have established that the tensor of the electric field gradient at the sites of the vanadium nuclei is axially symmetric and the symmetry axis is directed along the vanadium chains, i.e., along the [100] crystallographic axes. This demonstrates the predominance of the transition element chains in the formation of the electron structure of intermetallic compounds of the A-15 type. The quadrupole interaction parameter is $\nu_Q = 0.205 \pm 0.001$ MHz.

Within the limits of the experimental error, the Knight shift is also axially symmetric: its symmetry axis coincides with the corresponding axis of the tensor of the electric field gradient. The isotropic and anisotropic components of the Knight shift are, respectively, $K_{is} = 0.43 \pm 0.02\%$ and $K_{an} = 0.04 \pm 0.015\%$.

An analysis of the results obtained demonstrates why the Knight shifts deduced from the central components of the resonance spectrum do not agree with the shift deduced from the satellites.[6] Moreover, the observed temperature dependence of the width of the central component of the V^{51} line of V_3X intermetallic compounds[9] can be explained by an increase in the anisotropic component of the Knight shift which occurs when the temperature is lowered.

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161