V^{51} Knight Shift in the V_3Si Type of Compounds in the Normal State

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Gossard has observed in V_3Si the effect on the V^{51} Knight shift of the low-temperature structural transformation discovered by Batterman and Barrett. This effect can be explained in a simple model which assumes a fine d-band structure close to the Fermi level. This model has already given a fairly good explanation of the low-temperature lattice instability in the normal state.

I. INTRODUCTION

In the preceding paper[1] we have analyzed in a simple d-band model the paramagnetic susceptibility χ of the V_3Si type of compounds which have a high superconducting transition temperature T_c. The Fermi level should fall in a peak in the density of states and χ should consist of two main contributions:

$$\chi=\chi_0+\chi_d(T). \tag{1}$$

Here $\chi_d(T)$ is the strongly temperature-dependent Pauli contribution from the d electrons close to the Fermi level, and χ_0 is the nearly temperature-independent orbital contribution from all the occupied d-band states. In this paper we compute the Knight shift k_V at V^{51} nuclei, first in the cubic phase, and after in the tetragonal phase between T_c and the structural transformation $T_m(T_m>T_c)$.

II. KNIGHT SHIFT IN CUBIC PHASE

The Knight shift k_V at the vanadium nuclei contains a positive orbital contribution,[2] proportional to χ_0 and thus temperature-independent. The Pauli contributions from the d electrons contribute to k_V by the exchange polarization of the inner s core. This contribution is *negative* and proportional to $\chi_d(T)$. By neglecting the temperature-independent contribution due to the contact hyperfine interaction of the s electrons at the Fermi level with the nuclei, we can write

$$k_V=\beta\chi_0+\gamma\chi_d(T), \tag{2}$$

with $\beta>0$ and $\gamma<0$. Because of Eqs. (1) and (2), we see that the χ and k_V variations with the temperature are linearly related by

$$\Delta k_V=\gamma\Delta\chi. \tag{3}$$

This well-verified relation[2] makes it possible to determine experimentally γ. We find in V_3Si

$$\gamma\simeq-2.5 \text{ mole emu}^{-1}. \tag{4}$$

This value is much smaller than the one measured in pure vanadium metal,[3] where it is -15.5 mole $(\text{emu})^{-1}$. This may be due to the fact the d-atomic wave functions are more extended in space in V_3Si than in pure vanadium metal.[1] The result would be a decrease of the exchange interaction between the d electrons and the inner s core.

Now, by using our calculated values[1] of $\chi_d(T)$, the estimated value $\chi_0\simeq6\times10^{-4}$ emu mole^{-1}, and the measured values of k_V, we find that Eq. (2) is roughly valid for any temperature if we assume $\beta\simeq10$ mole $(\text{emu})^{-1}$, as an order of magnitude. [Our estimation of χ_0 and β is in good agreement with the values $\chi_0=5.2$ to 7.5×10^{-4} emu/mole and $\beta=11.25$ mole/emu, already found by Clogston, Gossard, Jaccarino, and Yafet[2] from NMR.]

III. EFFECT OF STRUCTURAL TRANSFORMATION ON KNIGHT SHIFT AT V^{51} NUCLEI

Let us consider the vanadium sites. In the cubic phase, all of them are equivalent. In the tetragonal phase, they can be divided into two families. The sites belonging to the first family are located in the chains running in the [100] direction which are assumed to elongate in the cubic to tetragonal transformation. We shall call them the c sites. The sites belonging to the second family are located in the chains running in the [010] and [001] directions which shorten in the transformation; we shall call them the a sites. The hyperfine structure magnetic field is not the same at the a and c sites. This leads to a splitting of the nuclear resonance lines, as observed by Gossard[4], between T_c and T_m.

The interatomic distances are weakly changed by the structural transformation, so the wave functions and the potentials undergo only small distortions. Thus we shall assume that the variation of β and γ in Eq. (2) can be neglected in first approximation. On the other hand, the electronic *distribution* in the d band, close to the Fermi level, is strongly affected by the structural transformation. In Ref. 1 we have described the fine d-band structure associated with the lattice distortion. The occupancy of the d band in the cubic phase is shown in Fig. 4 of Ref. 1. In the tetragonal phase, the electronic distribution in the two widest sub-bands is not appreci-

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[2] A. M. Clogston, A. C. Gossard, V. Jaccarino, and Y. Yafet, Rev. Mod. Phys. **36**, 170 (1964); Phys. Rev. Letters **9**, 262 (1962).
[3] L. E. Drain, Proc. Phys. Soc. (London) **83**, 755 (1964).
[4] A. C. Gossard, Phys. Rev. **149**, 246 (1966).

ably changed. But in the third sub-band, which contains very few electrons, this distribution is strongly perturbed. The peak at the bottom of this sub-band splits into a [100] peak and a [010]+[001] peak as shown in Fig. 6 of Ref. 1. The Fermi level E_F' lies between the bottoms E_{m1} and E_{m2} of these two new peaks. Numerical estimate in our model, for V_3Si, give $E_{m1}-E_{m2}\simeq 7.10^{-3}$ eV and $E_{m1}-E'_F\simeq 3.10^{-3}$ eV. At absolute zero, the contribution of this sub-band to the density of states at the Fermi level vanishes on the c sites. All the electrons of the sub-band are transferred to the a sites. On these sites, the Fermi level moves away from the peak in the density of states, at the bottom E_{m2} of the sub-band (Fig. 6 of Ref. 1). So the density of states at the Fermi level becomes $n_2(E_F')=Z/\pi|E_{m2}|\sin k_F'a$. In the cubic phase it was[5] $n(E_F)=Z/\pi|E_m|\sin k_Fa$. Because of the electrons transferred from the c sites to the a sites, we have $k_F'=\frac{3}{2}k_F$. As $E_{m2}\simeq E_m(1+\frac{1}{2}aq\epsilon)\simeq E_m(1+0.5\ 10^{-3})$, we get $n_2(E_F')\simeq\frac{2}{3}n(E_F)$. Of course, at the c sites we should get $n_1(E_F')=0$.

At finite values of the temperature, the [100] sub-band (Fig. 6 of Ref. 1) no longer remains empty. At temperatures lying between T_c and T_m, but not too close to T_m, the difference $E_{m1}-E_{m2}$ is of the same order of magnitude as kT. So the occupation of the c sites by electrons of the sub-band, although still reduced, can no longer be neglected.

We shall calculate the effect of the structural transformation first on the Pauli susceptibility $\chi_d(T)$, and then on the orbital susceptibility χ_0. Finally, the effect on k_V will be deduced from (2).

A. Pauli Susceptibility between T_c and T_m

The Pauli susceptibility per vanadium atom is, at the c sites,

$$\chi_d^{(c)}(T)=\mu^2n^{(c)}(T)/(1-Jn^{(c)}(T)), \tag{5}$$

where J arises from exchange interactions, μ is the Bohr magneton, and

$$n^{(c)}(T)=-\int_{E_{m1}}^{-E_{m1}}f'(E)n_1(E)dE. \tag{6}$$

At the a sites, it is

$$\chi_d^{(a)}(T)=\mu^2n^{(a)}(T)/(1-Jn^{(a)}(T)), \tag{7}$$

with

$$n^{(a)}(T)=-\int_{E_{m2}}^{-E_{m2}}f'(E)n_2(E)dE. \tag{8}$$

$n_1(E)$ and $n_2(E)$ are related[5] to $n(E)$ by

$$n_1(E)=\exp(aq\epsilon)n[E\exp(aq\epsilon)],$$
$$n_2(E)=\exp(-\tfrac{1}{2}aq\epsilon)n[E\exp(-\tfrac{1}{2}aq\epsilon)],$$

while $E_{m1}=E_m\exp(-aq\epsilon)$ and $E_{m2}=E_m\exp(\frac{1}{2}aq\epsilon)$. Of course, the Fermi level has the same value E_F' in Eqs. (5)–(8). This value is obtained, at any temperature, by writing the number of electrons in the sub-band as a constant. This gives

$$\int_{E_{m1}}^{-E_{m1}}f(E)n_1(E)dE+2\int_{E_{m2}}^{-E_{m2}}f(E)n_2(E)dE=3Q. \tag{9}$$

In all these equations, the distortion ϵ is a function of the temperature, numerically given by the curve in Fig. 7 of Ref. 1.

We did numerical calculations for $\mu^2n^{(c)}(T)$ and $\mu^2n^{(a)}(T)$. The results are shown in Fig. 1. These results hold only for $T>T_c$, because in the superconducting state the pairing causes the Pauli susceptibility to vanish.

We have seen that in our model the structural transformation is first order. Indeed, at $T=T_m$ we find very small discontinuities as shown Fig. 1. The order of magnitude of these discontinuities is about 10^{-6} emu mole^{-1}. Their smallness can be understood from the fact that at $T=T_m$ the residual distortion $\epsilon(T_m)$ is small (Fig. 7 of Ref. 1.) So the difference $E_{m1}-E_{m2}$ is small with respect to kT_m, and the temperature spreads the electrons almost equally between the a and c sites.

We see in Fig. 1 that $\mu^2n(T)$ slightly decreases on the a sites and much more on the c sites, when the temperature decreases from T_m to T_c. Numerically, we find, for the variation of $\mu^2n(T)$ from T_m to T_c, -0.12×10^{-4} emu mole^{-1} on the a sites, and -3.3×10^{-4} emu mole^{-1} on the c sites.

B. Effect of Structural Transformation on Orbital Susceptibility

To show this effect to be negligible, we shall use Eqs. (15)–(18) of Ref. 1. These give the orbital susceptibility χ_0 at absolute zero. When the lattice is distorted, Δ_1, Δ_2, k_1, k_2, and k_3 undergo small variations. By differen-

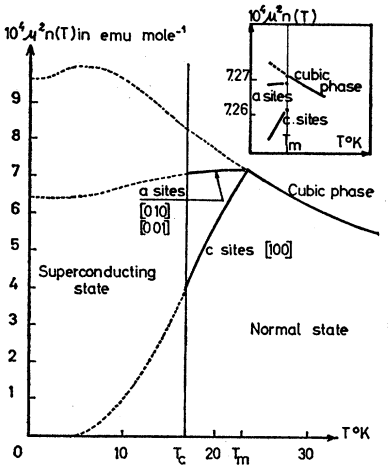

FIG. 1. Calculated temperature variations of $\mu^2n^{(c)}(T)$ and $\mu^2n^{(a)}(T)$, i.e., Pauli susceptibility without exchange at the c and a sites.

[5] J. Labbé and J. Friedel, J. Phys. Radium 27, 153 (1966).

tiating these four equations, we find

$$\delta\chi_0 = 3N\frac{4\mu^2}{3\pi}\left\{-\frac{4R_1\delta\Delta_1}{\Delta_1^2}-\frac{6R_2\delta\Delta_2}{\Delta_2^2}-\frac{4\delta(k_1a)}{\Delta_1\cos k_1a}+\left[\frac{4}{\Delta_1\cos k_2a}-\frac{6}{\Delta_2\cos k_2a}\right]\delta(k_2a)+\frac{6\delta(k_3a)}{\Delta_2\cos k_3a}\right\}, \quad (10)$$

$$E_m^{(1)}\sin k_1a\,\delta(k_1a) = E_m^{(2)} \times \sin k_2a\,\delta(k_2a) = E_m^{(3)}\sin k_3a\,\delta(k_3a). \quad (11)$$

The narrowest sub-band is nearly empty, in V_3Si. Thus k_1a is very small and, by (11), $\delta(k_2a)$ and $\delta(k_3a)$ are small with respect to $\delta(k_1a)$. Therefore, the last two terms in (10) can be neglected. On the other hand, the distortion ϵ being small, the sub-band widths only undergo small variations. We then have $\delta\Delta_1/\Delta_1 = \delta\Delta_2/\Delta_2 \simeq \frac{1}{2}aq\epsilon$ on the a sites and $-aq\epsilon$ on the c sites, with, in our case, $aq\epsilon \simeq 10^{-3}$. Therefore, the first two terms in (10) can also be neglected. Finally, as $k_1a \ll 1$, we get

$$\delta\chi_0 \simeq -3N(16\mu^2/3\pi)\,\delta(k_1a)/\Delta_1. \quad (12)$$

In (12), $\delta(k_1a)$ is not the same at the c and a sites. Even if χ_0 does not depend on the temperature, its variation $\delta\chi_0$ does depend on the distortion amplitude ϵ, which itself depends on the temperature T. More precisely, in (12), $\delta(k_1a)$ depends on the number of transferred electrons, thus on ϵ and finally on T.

Thus, between T_c and T_m, $\delta\chi_0$ is smaller than at $T=0$. Now, we shall give an estimate of $\delta\chi_0$ at absolute zero. On the c sites, the sub-band (Fig. 6 of Ref. 1) loses all its electrons, $\delta(k_1a) = -k_1a$ and thus, by (12) $\delta\chi_0 \simeq 3N(16\mu^2/3\pi)\,k_1a/\Delta_1$. On the a sites, the Fermi level moves away from the peak, $\delta(k_1a) = \frac{1}{2}k_1a$ and thus $\delta\chi_0 \simeq -3N(8\mu^2/3\pi)k_1a/\Delta_1$. Numerically, with $k_1a \simeq 2.8\times10^{-2}$ rad and $\Delta_1 = 0.5$ eV, we find that $\delta\chi_0$ is equal to -0.046×10^{-4} emu mole^{-1} on the a sites, and to 0.092×10^{-4} emu mole^{-1} on the c sites. The fact that, even at $T=0$, $\delta\chi_0$ is smaller than the change in $\mu^2n(T)$ from T_m to T_c can easily be understood. For it is only near the Fermi level that the occupancy of the d band is strongly perturbed by the structural transformation. Now, unlike $\chi_d(T)$, χ_0 depends on all the occupied states in the band, not only on these states which remain close to the Fermi level.

C. Knight-Shift Results

The Knight-shift variation when T decreases from T_m to T_c is given by $\delta k_V = \beta\delta\chi_0 + \gamma\delta\chi_d(T)$, from (2). The strongest effect comes from the second term. By taking into account the negative value of γ, given by (4), we see that k_V slightly increases on the a sites and much more on the c sites. Numerically, we find that, between T_m and T_c, k_V increases by 0.003% on the a sites, and by 0.08% on the c sites. Experimentally, Gossard[4] has found that on the a sites k_V increases by a quantity which is of the same order of magnitude as its experimental incertitude, i.e., 0.02%. On the c sites, he has found that k_V increases by $0.06\pm0.02\%$.

IV. CONCLUSION

Our model seems in reasonable agreement with Gossard's results. Here, we may notice that, if the [100] sub-band would not lose all its electrons, at zero temperature, i.e., if the Fermi level would stay in this sub-band, $\chi_d(T)$ would increase on the c sites. Thus k_V would decrease on these sites in disagreement with experiments. So Gossard's results seem to confirm the occurence of a Jahn-Teller type of effect with the complete cutoff of the occupied states of a d sub-band, as in Fig. 6 of Ref. 1.

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