SOME PROPERTIES OF SUPERCONDUCTING COMPOUNDS OF THE V₃Si TYPE

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SUPERCONDUCTING compounds with high transition temperatures are of such great practical importance that we already possess very much experimental information about them. Especially interesting experiments have been performed to compare the properties of substances that are similar in structure and chemical composition but exhibit very different superconducting transition temperatures T_c. It is the purpose of this experimental work to determine the structural properties that cause high transition temperatures; the importance of such investigations is obvious. Moreover, a number of very interesting features observed in the behavior of compounds having high T_c appear to indicate an unusual superconductivity mechanism that deserves the attention of both theorists and experimenters. We shall here discuss the results of some experimental investigations of V₃Si and similar compounds.

The superconducting transition temperatures of V₃X compounds are given in the following table. At room temperature all these compounds have a β-tungsten lattice structure. Batterman and Barrett[1] observed that in the range 20–30°K V₃Si undergoes a structural transformation from a cubic to a tetragonal lattice, and that within a few degrees below the transition point the tetragonal axial ratio c/a increases to the limit 1.0025. The experimental work shows that this is either a second-order transition or a first-order transition with a very small jump of the parameter c/a. Studies of V₃Ir ($T_c < 0.3°K$) have shown that no corresponding structural transformation occurs in this compound down to 4.6°K. On the other hand, a basis does exist for postulating[1] that Nb₃Sn ($T_c = 18°K$), like V₃Si, undergoes a structural phase transition at close to 35°K. One is therefore tempted very strongly to associate the high superconducting transition temperature with the structural transformation.

Anderson and Blount[2] have proposed the following explanation of this relationship. If the system has a very low optical phonon branch near the structural phase transition point, the effective interelectronic attraction resulting from the exchange of these excitations should be very strong and thus, of course, elevate the transition temperature. Let us consider to what extent a reduction of lattice vibration frequency affects the superconducting transition temperature T_c.

The Bardeen–Cooper–Schrieffer (BCS) superconductivity theory gives

$$T_e \sim \bar{\omega} e^{-\frac{\bar{\omega}^2}{\lambda}}, \tag{1}$$

where λ is a constant that depends particularly on the density of states at the Fermi surface, while the lattice vibration frequency $\bar{\omega}$ corresponds to a wave vector that is close to $2k_F$, where k_F is the Fermi wave vector (phonons of this frequency are mainly responsible for the attraction between electrons). It is easily seen that this formula is equally true for acoustic and optical phonons; the only difference lies in the constant λ.

Equation (1) is applicable when the exponential factor is very much smaller than unity. In all known instances we have $\exp(-\overline{\omega^2}/\lambda) \sim 10^{-2}$. In this region any reduction of $\bar{\omega}$ will elevate T_c. Let us consider two superconductors designated by the subscripts 1 and 2. From (1) we obtain

$$\frac{T_{c2}}{T_{c1}} = \frac{\bar{\omega}_2}{\bar{\omega}_1} \exp\left(\left[1 - \left(\frac{\bar{\omega}_2}{\bar{\omega}_1}\right)^2 \frac{\lambda_1}{\lambda_2} \right] \ln \frac{\bar{\omega}_1}{T_{c1}} \right). \tag{2}$$

If we take V₃Ir and V₃Si as the superconductors 1 and 2, respectively, with $T_{c1}/\bar{\omega}_1 \sim 10^{-3}$ for V₃Ir (corresponding to characteristic lattice vibrational frequencies of the order 300°K), it will follow from (2) that the observed transition temperature ratio ($T_{c2}/T_{c1} \sim 50$–60) can be accounted for through a frequency difference by a factor of only 1.5–1.6! In this estimate we have assumed equality for the constants λ_1 and λ_2, although a relatively small difference between them can even diminish the reduction of the frequency ω_2 that is required to account for the experimental value of T_{c2}/T_{c1}.

Therefore a large difference between the transition temperatures of two substances having similar structures is not especially surprising, because the temperature is strongly dependent on the values of the characteristic parameters. In addition, a recent investigation has shown[3] that in some samples of V₃Si no structural transformation occurs, but that the superconducting transition temperature remains approximately the same as in the transformed samples. Of course, the absence of a phase transition does not

	V₃Si	V₃Ga	V₃Ge	V₃Pt	V₃Co	V₃As	V₃Sb	V₃Au	V₃Ir
T_c, °K	17.1	16.5	6.0	2.8	<1	<1	<1	<1	<0.3

mean that the system contains no low phonon branches.

It follows from all of the foregoing discussion that although the large difference between the values of T$_C$ for V$_3$Si and V$_3$Ir can be explained without considerations involving the appearance of low phonon branches, there is still no basis for rejecting such a possibility. We feel that the question of the relationship between the structural transformation and superconductivity in V$_3$Si deserves detailed study.

The structural transformation is not the only singularity of V$_3$Si. In some very interesting experiments the velocity of sound was measured at temperatures from 4.2 to 300°K.[4] With decreasing temperature the crystal gradually loses its stiffness with respect to shear waves propagating in the [110] direction with [1$\bar{1}$0] polarization. The shear modulus corresponding to this deformation drops sharply with decreasing temperature (Fig. 1), and at 30°K becomes so small that the crystal is no longer transparent to these vibrations and the modulus must be measured indirectly. From 300° down to 4.2°K the shear modulus $c_{11} - c_{12}$ decreases by a factor of about 50. In [17] a great reduction of $c_{11} - c_{12}$ was observed even under constant stress.

One may presume that the reduction of $c_{11} - c_{12}$ and the structural transformation result from a loss of stability against shear deformation. However, it was shown in [2] that in crystals of the V$_3$Si type this transformation can only be of the first-order type.

We are immediately confronted with the question whether the high value of T$_C$ in the case of V$_3$Si is related to its particular elastic properties. First of all, it is clear that the effective attraction between electrons results from their interaction with lattice shear vibrations. The interaction can be described by the expression $gp_i(u_{ik}/2m)p_k$, where p_i is an electron momentum component, m is the electron mass, u_{ik} represents the deformation tensor, and g is a dimensionless constant of the order of unity.*

It is also proved easily that for normal values of the elastic moduli and a Fermi momentum of the order $\hbar/a$, where a is the lattice constant, the aforementioned attraction is of the same order as the attraction resulting from the ordinarily considered interaction ϵu_{ii}.

Figure 1 shows that at T$_C$ the shear parameter has about $\frac{1}{20}$ of its normal value. As a result, lattice waves propagating in directions very close to [110], [101], and [011] exhibit anomalously low velocities and the exchange of these phonons is responsible for a strong attractive force. Therefore, despite the relatively low statistical weight of these phonons by virtue of the exponential dependence of T$_C$ on $\bar{\omega}$, such a large change in the elastic moduli can greatly elevate the
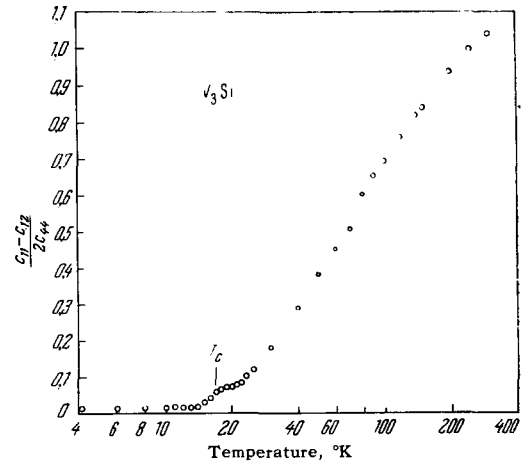

FIG. 1. Dependence of $c_{11} - c_{12}/2c_{44}$ on temperature.

transition temperature. A similar sharp reduction of the shear modulus was recently observed in Nb$_3$Sn single crystals.[15]

We note that a substance for which $c_{11} - c_{12} = 0$ exhibits highly anisotropic elastic properties, while $c_{11} - c_{12} = 2c_{44}$ holds for isotropic substances. Therefore $2c_{44}/(c_{11} - c_{12})$ can serve as a measure of elastic anisotropy (anisotropy factor).

V$_3$Si exhibits high anisotropy of its superconducting properties as well as of its elastic properties. It has been shown experimentally[5] that when a stress is applied in the [100] direction the transition temperature varies by about -5×10^{-4} deg/atm, whereas a stress along [111] or hydrostatic compression does not seriously affect T$_C$. (According to [6], under hydrostatic compression the change of T$_C$ is -2×10^{-5} deg/atm.) It can be assumed that such highly anisotropic dependence of T$_C$ on stress is linked to the anisotropy of the elastic properties. The ordinary theory of superconductivity leads to the following dependence of T$_C$ on the deformation tensor in cubic crystals:*

$$T_c = T_c^0(1 + \alpha u_{ll}) \qquad (2a)$$

(where α is a dimensionless constant). According to this expression T$_C$ would depend only on the relative change of volume.

A very simple analysis shows that for stress along [100] and [111] and for hydrostatic compression the volume changes (with σ representing stress) would be $\sigma/c_{11} + 2c_{12}$, $\sigma/c_{11} + 2c_{12}$, and $3\sigma/c_{11} + 2c_{12}$, respectively, and would thus be of the same order. Therefore, the fact that stress along [100] is accompanied by a change of T$_C$ that is an order above the corresponding change for stress along [111] or for hydrostatic compression cannot be accounted for by means of (2a). We are led to postulate that T$_C$ varies with shear deformations as well as with volume changes.

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*This expression describes essentially the relation between the effective mass and the deformation; in general $\partial m/\partial u_{ik} \approx m$, so that g is of the order of unity.

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*The small axial ratio (c/a $\approx$ 1.0025) resulting from the aforementioned structural transformation can evidently be disregarded.

It is easily shown that for stress along [100] we have

$$u_{xx} = \sigma \frac{c_{11}+c_{12}}{c_{11}+2c_{12}} \frac{1}{c_{11}-c_{12}} \,, \Bigg\}$$
$$u_{yy} = u_{zz} = \frac{1}{2} \left\{ -\sigma \frac{c_{11}+c_{12}}{c_{11}+2c_{12}} \frac{1}{c_{11}-c_{12}} + \frac{\sigma}{c_{11}+2c_{12}} \right\} \Bigg\} \quad (3)$$

and for hydrostatic compression we have

$$u_{xx} = u_{yy} = u_{zz} = \frac{\sigma}{c_{11}+2c_{12}} \,, \quad (4)$$

while for stress along [111] we have

$$u_{xx} = u_{yy} = u_{zz} = \frac{\sigma}{3(c_{11}+2c_{12})} \,, \quad u_{xy} = u_{xz} = u_{yz} = \frac{\sigma}{3c_{44}} \,. \quad (5)$$

When we compare (3), (4), and (5) we find that in the first instance, where T_C depends most on stress, anomalously large deformations occur corresponding to shears along [110]. These large deformations follow from (3) when we recall that $c_{11} - c_{12}$ has the very small value $(5 \times 10^{-2})2c_{44}$. The ratio of deformations in this case to deformations under hydrostatic compression is of the order $\frac{c_{11}+c_{12}}{c_{11}-c_{12}} \sim 50$.

When we consider that the dependence of the transition temperature on stress along [100] is about 25 times greater than its dependence on hydrostatic pressure, we easily arrive at the conclusion that shear deformations affect T_C as greatly as do any changes of volume. All of the foregoing indicates extreme anisotropy of the superconducting state of V_3Si.

We note also that the large anisotropy of the electronic properties of V_3Si and similar compounds evidently results from the character of their structure.[7] In V_3X alloys the vanadium atoms are arranged in arrays of straight lines in $\langle 100 \rangle$ directions, and the separations of neighboring atoms along any single straight line are very much smaller than the separations of the lines themselves (Fig. 2a). If we now consider the 3d bands of vanadium based on the tight binding approximation with consideration of only nearest-neighbor interactions, we easily deduce that only the states of atoms along a single line can combine, so that electron motion is here quasi-one-dimensional. The Fermi surface now consists of (100) planes and is extremely anisotropic, as shown in Fig. 2b.

Weger,[7] who is responsible for the foregoing treatment, pointed out that the quasi-one-dimensional character of electron motion in V_3X compounds could have been accounted for by several experimentally observed peculiarities of electron properties in these
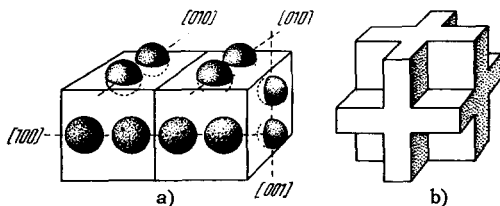
compounds. We refer to the strong temperature dependence (in the normal state) of the Knight shift[8] (Fig. 3), of electronic magnetic (or spin) susceptibility[8,9] (Fig. 4), and of the quantity $1/T_1T$, where T_1 is the longitudinal relaxation time of nuclear magnetic resonance[7] (Fig. 5). All these results can be regarded as evidence for the strong temperature dependence of the density of states on the Fermi surface. Weger postulates that this temperature dependence results from electron-phonon interactions, which in the one-dimensional case lead to a very much more drastic renormalization of the electron self-energy than in the three-dimensional case; the correction ratio of the one- and three-dimensional cases is of the order of E_F/T_C.

Figures 3 and 5 show that in a number of V_3X alloys the observed temperature dependence of the Knight shift and of $1/T_1T$ becomes stronger as we go to higher superconducting transition temperatures. The same applies to the temperature dependence of magnetic susceptibility.[9]

In the light of Weger's treatment the foregoing situation is quite rational, since the effective electron-electron attraction and the temperature dependence of the density of states on the Fermi surface have a single cause—the electron-phonon interaction. We also note that since we have postulated that the quasi-one-dimensional character of 3d-electron motion is responsible

FIG. 2. a) Crystalline structure of V_3X compounds; b) Fermi surface of vanadium 3d electrons in the tight binding approximation.
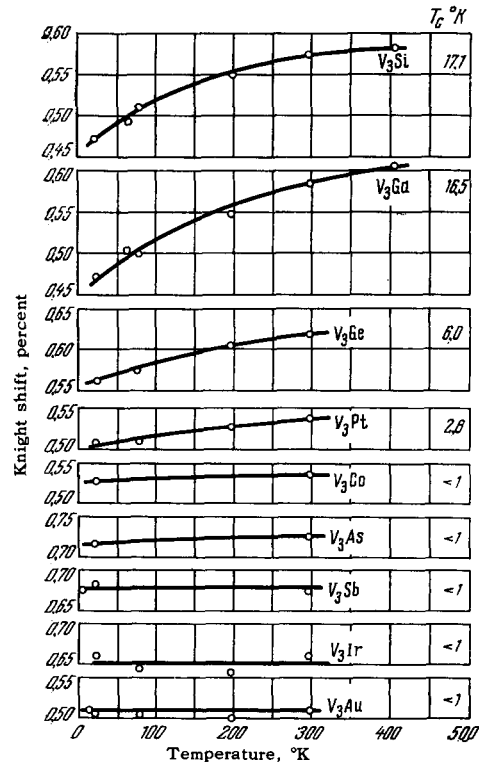

FIG. 3. Temperature dependence of the Knight shift for $T > T_c$ in V_3X compounds (with resonance in the V^{51} nucleus). The value of T_c for each compound is shown on the right-hand side of the graph.
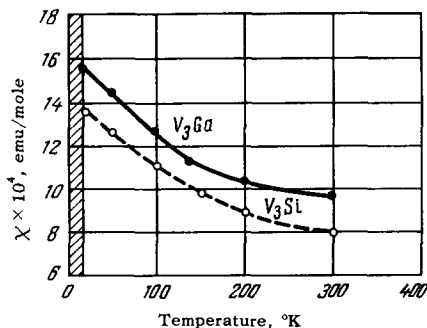
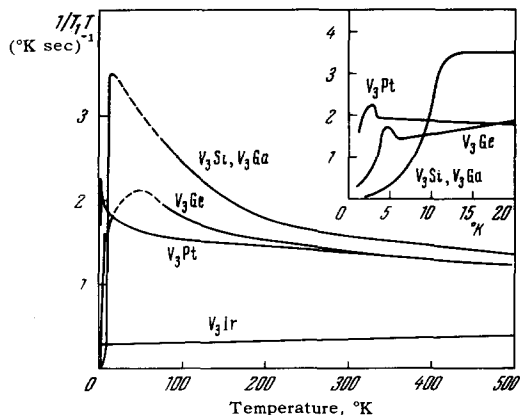FIG. 4. Temperature dependence of magnetic susceptibility in V_3Si and V_3Ga for $T > T_c$.

FIG. 5. Dependence of $1/T_1T$ on temperature for different V_3X compounds. T_1 is the longitudinal relaxation time.
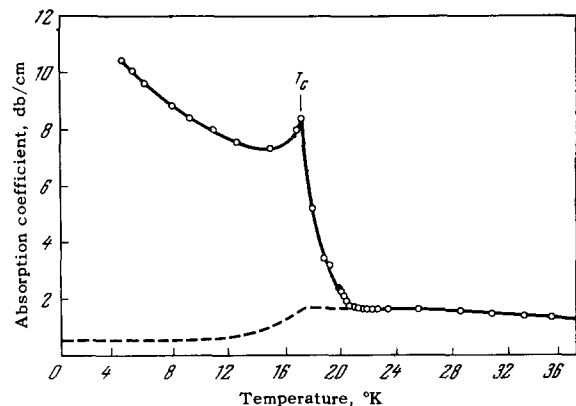

FIG. 6. Sound absorption coefficient vs temperature for 310-Mc longitudinal wave traveling along [110] direction. The dashed line represents the temperature for "ordinary" superconductors.

for the exceedingly strong electron-phonon interaction in V_3Si and V_3Ga, we should also assume that in V_3Ir, for example, this "one-dimensionality" of electron motion is considerably smeared, i.e., the wave functions of electrons located on different straight lines will overlap considerably. Therefore the analysis of the character of 3d wave-function overlapping in different V_3X compounds is obviously of great interest.

The stability of metal lattices with anisotropic Fermi surfaces has been considered by Labbé and Friedel,[16] who have shown that in a model of the electron spectrum that coincides essentially with Weger's model a cubic lattice is unstable against shear deformations defined by the modulus $c_{11} - c_{12}$ at low temperatures; a cubic lattice then becomes tetragonal. This instability greatly reduces the value of $c_{11} - c_{12}$ and causes a first-order tetragonal transition at a quite low temperature, with a small change of c/a. Labbé and Friedel identify this transition with the aforementioned structural transition in V_3Si and Nb_3Sn. Their model thus provides a unified explanation for the observed reduction of the shear modulus and for the structural transformation. However, they did not consider the superconductivity of these compounds. We discuss, finally, the extremely interesting experiments on sound absorption in V_3Si that are reported in [4]. Figure 6 shows the temperature dependence

exhibited by the absorption coefficient for a longitudinal wave traveling in the [110] direction. Measurements were also obtained for the absorption of transverse waves along [110], and for both transverse and longitudinal waves along [001; in these instances the curves resemble Fig. 6 qualitatively. The most striking feature is the sharp divergence between the experimental results and the predictions of the BCS theory (the dashed curve). We recall that for a number of "ordinary" superconductors the BCS theory is in excellent agreement with experiment.[10] An interesting feature of the experimental curve considered here is that its maximum is located at $T \simeq T_c$. In ordinary superconductors one does not observe this maximum. Although a superconducting transition, like any second-order phase transition, is accompanied by enhanced sound absorption (close to the transition point) that is associated with an increase of the relaxation time and of the level of thermal fluctuations exhibited by a characteristic transition parameter[11-13] (which for semiconductors is the wave function in the Ginzburg-Landau theory), in superconductors this anomalous absorption becomes appreciable in only a very narrow temperature range about the transition point with its width represented by the ratio $\Delta T/T_c \sim (T_c/E_F)^4$.[14] Since $E_F \sim 10$ deg, we find that even at $T_c \sim 20°$ this width is of the order 10^{-11}, and it would appear that there is not the slightest possibility of detecting in superconductors the anomalous sound absorption that characterizes other second-order phase transitions. The experimental results obtained for V_3Si are thus all the more interesting.

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