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Lattice Instability of High-Transition-Temperature Superconductors. I. Polycrystalline A-15 Compounds

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The A-15 (β-tungsten) structure compounds Nb_3Sn, Nb_3Al, Nb_3Ga, V_3Si, and V_3Ga, which are all superconducting above 14°K, have been found to exhibit elastic softening on cooling. The anomalous temperature dependence of the elastic moduli disappears in the superconducting state. This unusual behavior does not occur for the isostructural compounds V_3Ge and Nb_3Ge, which have comparatively low transition temperatures ($T_c \sim 5$–7°K).

INTRODUCTION

THE A-15 (β-tungsten) structure compounds Nb_3Sn, Nb_3Al, Nb_3Ga, V_3Si, and V_3Ga comprise a large portion of those materials known to be superconducting above approximately 14°K.[1] A large low-temperature lattice instability has recently been reported[2] for V_3Si. In this compound the shear modulus for ultrasonic waves propagating along [110] with polarization along [1$\bar{1}$0] decreases very rapidly on cooling. In the present work we show that the anamalous behavior of elastic softening on cooling is characteristic of all of the high-transition-temperature superconductors mentioned above. A discussion of the possible causes and some of the consequences of the elastic softening are given in the following sections.

EXPERIMENTAL PROCEDURE AND RESULTS

Pulse-echo measurements of 20-Mc/sec sound-wave velocities have been made in the above materials between 300 and 4.2°K using the McSkimin pulse-superposition method.[3] The longitudinal V_L and shear V_S velocities are related to the compressional L and shear G elastic moduli by $L = V_L^2\ \rho$, $G = V_S^2\ \rho$, where ρ is the material density.

The materials were prepared by the reaction of the elemental constituents in water-cooled silver boats[4] or refractory crucibles. Because of selective vaporization and the possibility of a peritectic formation,[5] it is difficult to obtain stoichiometric, single-phase samples of these compounds. To induce the growth of single crystals a subsequent "floating-zone" pass was made, but this attempt was successful only for V_3Ge and V_3Si. In all other cases the use of polycrystalline samples set several limitations upon the results of these measurements. One limitation arises from the loss of essentially all information on the elastic anisotropy. A further restriction lies in the fact that a large temperature variation of the velocity of a particular mode may not be detected in the polycrystalline average. For V_3Si (see below) this latter limitation is clearly evident. The superconducting transition temperatures, determined from inductance measurements, were found to be somewhat lower than the reported values for these compounds.

In Table I we give the velocities of the longitudinal V_L and shear V_S waves for these compounds as well as the fractional change in velocity between 4.2 and 300°K. Depending on the defect state of the sample (porosity and second-phase amounts) one can attain a measurement precision of one part in 10^3 to 10^5, but there is little significance in establishing the accuracy to better than 1 to 2% since the measured value depends to this extent on the state, as prepared, of the polycrystalline sample. In many cases the attenuation of shear waves was too large to permit velocity measurements. The temperature dependences of the velocities for some of the compounds are shown in Fig. 1.

DISCUSSION

For the compounds with high superconducting transition temperatures ($T_c > 14$°K) the velocities (and elastic moduli) decrease on cooling. The isostructural compounds V_3Ge and Nb_3Ge, which have comparatively

TABLE I. Sound velocities in polycrystalline A-15 superconducting compounds.

	T_c(K°)	V_L(300°K) (10^5 cm/sec)	V_S(300°K)	$\dfrac{\Delta V_L}{V_L}$[b]	$\dfrac{\Delta V_S}{V_S}$[b]	Calculated Debye temperature (°K)
Nb_3Sn	17.4	5.16	3.1	−4%	−5%	370
Nb_3Al	17.7	5.76	...	−2%	...	...
V_3Si	17.0	7.09	3.76	−18%	−2½%	530
Nb_3Ga	15.3	5.87	...	[c]	...	...
V_3Ga	14.2	5.61	...	−4%	...	...
V_3Ge[a]	6	6.53	3.195	+2½%	+½%	478
Nb_3Ge	5	5.78	2.90	+1%	+1%	378

[a] For propagation along [001].
[b] $\Delta V/V = [V(4.2°K) - V(300°K)]/V(300°K)$.
[c] For Nb_3Ga, the softening occurred below ~30°K. Since this sample was found to contain about 50% of a second phase, the significance of this behavior is in doubt.

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[1] The only other materials known to be superconducting above 14°K occur as a range of composition in the NbC-NbN alloy system. We have not succeeded in making sound-velocity measurements in sintered samples of these alloys which had been kindly loaned to us by J. Remeika.

[2] L. R. Testardi, T. B. Bateman, W. A. Reed, and V. G. Chirba, Phys. Rev. Letters **15**, 250 (1965).

[3] H. J. McSkimin, J. Acoust. Soc. Am. **33**, 12 (1961).

[4] H. F. Sterling and R. W. Warren, Metallurgia **67**, 301 (1963).

[5] Only the Nb-Sn, V-Si, and V-Ga phase diagrams are known with some certainty.

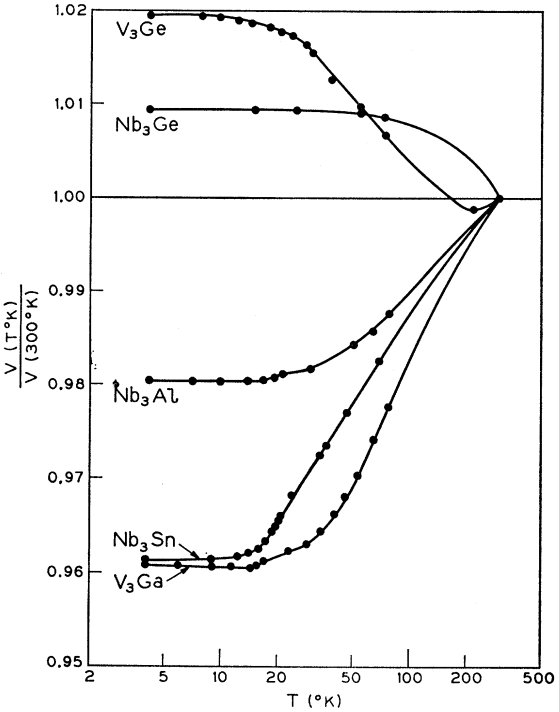

FIG. 1. The temperature dependences of the sound velocities in A-15 structure compounds. For V_3Ge the data are for shear waves propagating along [001]. All other data are for longitudinal waves in polycrystalline samples.

low transition temperatures ($T_c \sim 5$ to 7°K), exhibit the normal stiffening with cooling at the lower temperatures. Near room temperature, V_3Ge exhibits the anomalous temperature dependence of velocity similar to the high T_c compounds. However, the velocities attain minimal values below 300°K and the normal temperature dependence occurs at low temperatures. Further investigation of this behavior is in progress.

The magnitude of the softening which occurs in the high T_c superconductors is best judged from a comparison with the results of polycrystalline V_3Si. Studies[2] of the elastic moduli in a single crystal of this material showed that the restoring force for a [110] shear wave with [1$\bar{1}$0] polarization decreased by a factor of 10 between 300 and 25°K and fell to near-zero magnitude in the superconducting state. From the calculated Voigt and Reuss average elastic moduli of a polycrystalline sample[6] the shear-wave velocity in polycrystalline V_3Si should show a reduction between the limits of 30% (Voigt) and 160% (Reuss) from 300 to 20°K. The small experimental value for the reduction in velocity ($\sim 2\frac{1}{2}\%$) may result because the soft shear wave is strongly attenuated or because the crystallite size is not small compared to the sound wavelength. Both of these conditions violate the assumptions with which the average moduli are calculated. Therefore, our results cannot preclude the existence of a similar large selective-mode softening in the other high T_c compounds.[7] Table I also lists the Debye temperatures calculated from the polycrystalline elastic moduli in the manner proposed by Anderson.[8] For V_3Si, the room-temperature moduli were used.[9] In all other cases the 4.2°K moduli were used. For Nb_3Sn, Morin and Maita[10] have obtained a Debye temperature of 290°K from specific-heat measurements. Although this discrepancy could indicate that a much larger lattice softening occurs than is observed ultrasonically in the polycrystalline samples (as in V_3Si), the evidence is not conclusive.

The elastic softening which occurs on cooling represents, in a qualitative sense, a lattice instability detectable at room temperature which is apparently related to the occurrence of high-temperature superconductivity.[11] Although the general lowering of the lattice-mode frequencies with decreasing temperature would be of importance for the superconducting state, a quantitative estimate of this importance requires at least a knowledge of the phonon dispersion out to those frequencies ($\sim 10^{12}$ cps) where the density of phonon states would be large. Such measurements are beyond the range of ultrasonic techniques. However, if the softening does occur out to these frequencies, one can expect an anomalous temperature dependence of those properties which are determined by the velocities (or vibrational amplitudes) of these phonons, particularly if large selective-mode softening occurs. These include, for example, the specific heat and the electrical and thermal resistivities, all of which would decrease, on cooling, at a rate slower than that expected for a normal lattice in which softening does not occur.[12] Anomalies of this nature have, in fact, been reported in the specific heat of V_3Si [13] and the electrical resistivity of Nb_3Sn [14] but no numerical estimates of the softening effects can reliably be made.

For the high T_c compounds, the temperature dependence of the sound velocities are comparatively

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[6] The Voigt and Reuss averages are obtained by averaging the strain and the stress, respectively, and give the upper and lower limits for a polycrystalline sample. For the longitudinal waves in V_3Si (which are not highly attenuated) the calculated limits, 9% and 22%, do include the experimental value.

[7] A large selective-mode softening similar to that in V_3Si has now been observed in single-crystal Nb_3Sn by K. R. Keller and J. J. Hanak, Phys. Letters **21**, 263 (1966).

[8] O. L. Anderson, J. Phys. Chem. Solids **24**, 909 (1963).

[9] Further results based on the temperature dependence of the single-crystal elastic moduli for V_3Si are given in the following paper.

[10] F. J. Morin and J. P. Maita, Phys. Rev. **129**, 1115 (1963).

[11] In support of this relation is the additional experimental result that the substitition of 3 at.% Ti for V in V_3Si lowers T_c by 3°K and reduces the magnitude of the softening by a factor of 3.

[12] For soft shear waves the expected anomaly in the electrical resistivity would necessarily result from high-frequency phonons, since long-wavelength transverse waves do not scatter electrons. See, for example, A. H. Wilson, *The Theory of Metals* (Cambridge University Press, New York, 1958), p. 256.

[13] J. E. Kunzler, J. P. Maita, H. J. Levinstein, and E. J. Ryder, Phys. Rev. **143**, 390 (1966).

[14] D. Woodard and G. Cody, RCA Rev. **25**, 393 (1964).

large, as well as anomalous in sign just above T_c. In the superconducting state the temperature dependences are greatly reduced (see Fig. 1) and for V_3Ga and Nb_3Al a small negative slope generally expected for materials in this temperature range occurs. For Nb_3Sn, the broad transition to superconductivity was also observed in the inductance measurement of T_c.

The disappearance of the large temperature dependence of the elastic moduli below T_c suggests that the anamolous softening contribution is electronic in nature. The thermodynamic relation between the internal energy U and the adiabatic elastic modulus M for a given strain ϵ is given by $M=\partial^2U/\partial\epsilon^2$ at constant entropy. The temperature-dependent electronic contribution to U is proportional to the density of states at the Fermi energy and a large modulus temperature dependence of either sign can result from unusual (strain-sensitive) structure in the electronic density-of-states curve.[15] Calculations of the temperature dependence of M in terms of band-structure parameters have been made by Bernstein.[16] These results show that the elastic behavior which occurs in the high T_c compounds could be explained by a Fermi level which is coincident with a sharp peak in the density of states. Such an occurrence would also give rise to a large temperature dependence of the paramagnetic susceptibility.[16] This latter behavior has been reported[17] for several of the high T_c compounds, and an explanation based in part upon an assumed peak in the undressed density of states was given by Clogston and Jaccarino.[18] However, no reliable estimate (using Bernstein's calculations) for the temperature dependence of M for these materials can be made from existing information. Furthermore, the large phonon enhancement of the electron density of states in these compounds, which has been discussed by Clogston,[19] may lead to non-negligible effects upon the sound velocity.

At low temperatures (~20°K), V_3Si undergoes a structural transformation[20] which gives rise to a large increase in the high-frequency ultrasonic attenuation. For the polycrystalline samples used in the present studies, the large attenuation (at all temperatures) made it impossible to determine whether structural transformations occurred in any of the compounds studied.

The sound-velocity measurements in the high-transition-temperature superconductors show an anomalous behavior characteristic of a lattice instability. However, because of the polycrystalline nature of the samples one cannot obtain the detail or accuracy of data which is desirable for analysis. A fuller discussion of the softening is given in the following paper, which presents the single-crystal elastic-moduli results for V_3Si.

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[15] The presence of strain-sensitive structure in the density-of-states curve has also been suggested from the measured stress dependences of the specific heat (see Ref. 13) and the superconducting transition temperature [M. Weger, B. G. Silbernagel, and E. S. Greiner, Phys. Rev. Letters **13**, 521 (1964)].

[16] B. T. Bernstein, Phys. Rev. **132**, 50 (1963).

[17] Data of H. J. Williams and R. C. Sherwood given in Ref. 18.

[18] A. M. Clogston and V. Jaccarino, Phys. Rev. **121**, 1357 (1961). The importance of the large density of states for the anomalous elastic behavior could be established from measurements of NbN-NbC alloys which have high T_5's and low densities of states. See Ref. 1.

[19] A. M. Clogston, Phys. Rev. **136**, A8 (1964).

[20] B. W. Batterman and C. S. Barrett, Phys. Rev. Letters **13**, 390 (1964).