LATTICE INSTABILITY OF V_3Si AT LOW TEMPERATURES

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We have obtained evidence of an unusually large instability in the V_3Si lattice at low temperatures for shear waves propagating along the [110] direction with [$1\bar{1}0$] polarization. The shear modulus for this mode falls from a value typical of the metallic state at room temperature to near zero magnitude in the superconducting state. Both the structural[1] and superconducting transitions have marked effects upon the rate of softening with decreasing temperature.

The sound velocity and attenuation in a crystal[2] of V_3Si have been investigated in the temperature range of 4.2 to 300°K. The velocity measurements, made between 20 and 60 Mc/sec with the McSkimin pulse superposition technique,[3] were performed with longitudinal and shear waves propagating along [001] and [110] directions. The polarization directions of the shear waves were [110] and [001], respectively. From three of the velocity measurements the elastic moduli c_{11}, c_{12}, and c_{44} for this cubic (β-tungsten) crystal were obtained using standard expressions.[4] A fourth (redundant) measurement showed the internal consistency of the data to be better than one part in 1500 over the entire temperature range of the measurements. The accuracy was ±0.1%.

The measured velocities at room temperature and the calculated elastic moduli are given in Tables I and II.

On cooling from 300 to 4.2°K we observe reductions in c_{11} and c_{44} by the amounts 37.4 and 5.8%, respectively. This softening is contrary to the slight (1-5%) increase in elastic moduli generally observed with similar cooling for a normal "stable" lattice. A far larger instability occurs for shear waves propagating along [110] with [$1\bar{1}0$] polarization. The stiffness coefficient for this mode is given by $(c_{11}-c_{12})/2$. In Fig. 1 we show the temperature dependence of this quantity divided[5] by c_{44} which, itself, is relatively temperature independent. As the temperature is lowered, this stiffness parameter falls by a factor of 10 between room temperature and 25°K. Between 80 and 25°K the decrease occurs at a rate which would lead to the vanishing of the restoring force for the shear deformation at ~20°K. Below 22°K, however, the slope is reduced and some, but not complete, stabilization occurs.

In the superconducting state (T_C = 16.9°K) two marked changes occur. The first is a further reduction of the shear stiffness by a factor of 4 to 5, giving it a small positive value which differs from zero by only the magnitude of the experimental error. This reduction occurs continuously within three degrees below T_C. The second change is, perforce, the complete arrest of the growing lattice instability below 14°K. The changes in the elastic moduli c_{11} and c_{44} from the normal to the superconducting states are −1.33 and +0.25%, respectively. Even for these comparatively stable moduli the changes are about four orders of magnitude larger than those observed in tin.[6]

The ultrasonic attenuation has been studied using 20- to 500-Mc/sec longitudinal and shear waves in [110] and [001] directions. Although the magnitude of the attenuation depended upon each of these variants, the general features

Table II. Elastic moduli (10^{12} dynes/cm^2) at 300°K.

c_{11}	c_{12}	c_{44}
2.870	1.202	0.8096

Table I. Sound velocities at 300°K.

Mode	Propagation direction	Polarization direction	Velocity (10^5 cm/sec)
Longitudinal	[001]	[001]	7.097
Longitudinal	[110]	[110]	7.066
Shear	[001]	[110]	3.769
Shear	[110]	[001]	3.767

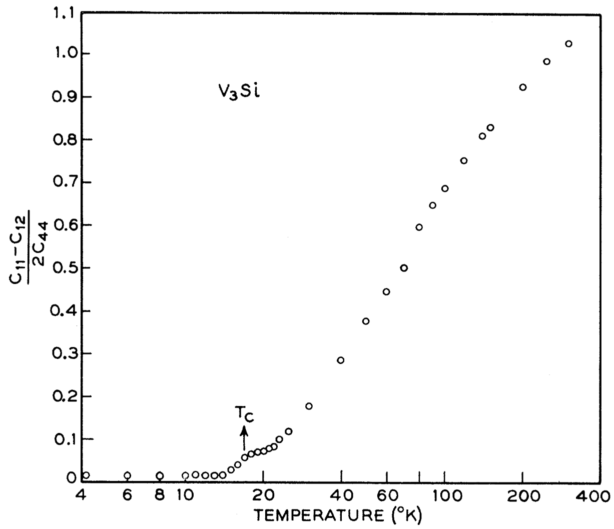

FIG. 1. The stiffness parameter $(c_{11}-c_{12})/2c_{44}$ versus temperature.

shown in Fig. 2 were obtained in every case. On cooling below 22°K the attenuation increases very rapidly to a maximum at the superconducting transition temperature. A minimum occurs below T_c followed by a comparatively gradual increase. The electronic component of the attenuation (which vanishes exponentially with temperature below T_c) has been calculated to be less than 20% of the observed attenuation at T_c. The behavior below 20°K, therefore, is almost entirely anomalous in nature. The striking feature of the attenuation is the marked arrest of its increase on cooling through T_c.

The results of the ultrasonic studies can be correlated, in part, with the occurrence

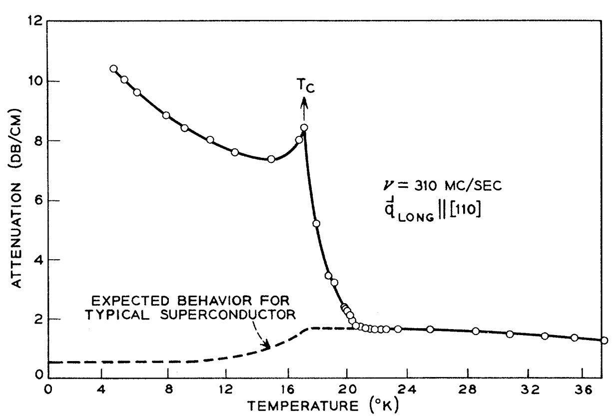

FIG. 2. Ultrasonic attenuation versus temperature for 310-Mc/sec longitudinal waves propagating along [110].

of a structural transformation in V_3Si recently reported by Batterman and Barrett.[1] As the temperature is lowered, the growing lattice instability becomes so large as to require some new occurrence to avoid the vanishing of the shear modulus $(c_{11}-c_{12})/2$. The partial stabilization that occurs around 22°K marks the onset of the reported transformation. The shear mode whose amplitude is increasing as a result of this instability represents, in fact, a form of deformation consistent with what is needed to give rise to the domain structure that occurs in the transformed state.

The onset of this transformation also introduces a mechanism for ultrasonic attenuation, but the nature of this mechanism has not been established. The arrest in the rate of increasing attenuation below T_c suggests that the transformation, itself, is arrested at T_c.[7] If the increasing instability of the soft shear wave $(c_{11}-c_{12})/2$ represents a driving force for this transformation, the stabilization of that stiffness parameter somewhat below T_c would also suggest an arrest of the transformation.[8]

However, the further reduction of $(c_{11}-c_{12})/2$ which commences with the onset of superconductivity is apparently related to an effect at T_c due to the structural transformation. The change in the modulus $(c_{11}-c_{12})/2$ (as well as c_{11} and c_{44}) is far too large to be accounted for by the disappearance in the superconducting state of the small electronic contribution to the crystal stiffness.[9] Furthermore, such stiffness contributions should be proportional to the square of the sound frequency, but no dispersion in the sound velocities was found to within one part in 5000 between 20 and 60 Mc/sec. Thermodynamic arguments[10] show that no change will occur in $(c_{11}-c_{12})/2$ for a simple and reversible superconducting transition. Thus, the large change observed in $(c_{11}-c_{12})/2$ presumably indicates a modification of the temperature dependence of the structural transformation at T_c.

Finally, it should be noted that the modulus for the [110] "soft" shear wave has been calculated from the velocities of other waves in other directions. All attempts to obtain its value directly using the [110] shear wave have failed below 30°K even at the lowest frequencies. The crystal is opaque for this wave.

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Clogston, and J. E. Kunzler for helpful discussion.

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

[2]E. S. Greiner and H. Mason, Jr., J. Appl. Phys. 35, 3058 (1964), give details of crystal preparation.

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

[4]W. P. Mason, Physical Acoustics and the Properties of Solids (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1958), pp. 370-71.

[5]$(c_{11}-c_{12})/2c_{44}$ is the reciprocal of the elastic anisotropy factor. (See reference 4, p. 357.) The value of unity for this factor near room temperature indicates glasslike elastic isotropy. In the superconducting state the anisotropy is probably the largest reported for any crystal.

[6]W. P. Mason and H. E. Bommel, J. Acoust. Soc. Am. 28, 930 (1956).

[7]The anomalous attenuation was not observed in a crystal in which no structural transformation was found from x-ray studies.

[8]B. W. Batterman has recently found that on cooling through T_c the growing deformation of the transformed lattice is arrested. From specific-heat data J. E. Kunzler and coworkers have arrived at similar conclusions (private communications). However, sluggish transformations, occurring continuously between 4 and 30°K, are occasionally observed.

[9]Reference 4, p. 325.

[10]Reference 4, p. 346.

ANTIFERROELECTRIC PHASE TRANSITION IN COPPER-FORMATE TETRAHYDRATE*

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Copper formate tetrahydrate $Cu(HCOO)_2 \cdot 4H_2O$ has been found by Kiriyama, Ibamata, and Matsuo[1] to have a layer structure in which layers of H_2O are sandwiched between layers of copper formate in the (001) plane. The symmetry is $P2_1/a$, $a = 8.18$, $b = 8.15$, $c = 6.35$ Å. Several investigators[2-4] published descriptions of the antiferromagnetic transition at about 17°K in this crystal. While attempting to determine hydrogen positions by neutron diffraction at room temperature, preliminary to investigating the magnetic structure, some water hydrogens were found to be disordered.[5] This stimulated us to measure the dielectric properties as a function of temperature. A preliminary check showed an anomalous dielectric constant as high as 400 at room temperature in an (010) plate. This publication reports that the crystal appears to be antiferroelectric due to hydrogen motion. It has a typical antiferroelectric behavior comparable to perovskite-type antiferroelectrics. In addition, unlike previously discovered antiferroelectrics, large single crystals can easily be grown and detailed experiments carried out. Antiferroelectric antiferromagnetism can be expected in this crystal below 17°K.

Single crystals were grown from aqueous solution by slow evaporation of water. (100) and (010) plates were cut from the single-crystal ingot by the wet-thread method and polished by fine emery paper. Thin "as-grown" (001) plates were obtained in a certain condition of crystal growth. The plates were about 0.4 mm thick. Electrodes were air-drying conductive silver coatings painted on the crystal surfaces to eliminate any gap between the crystal surface and the electrode. Moreover, crystals were coated by an insulating spray coating to avoid contact with air which would cause rapid dehydration.

Figure 1 shows the dielectric constant at low ac amplitude and 1000 cps versus temperature. As the temperature is decreased, the dielectric constant of the (010) plate rises to a peak of 1500 at −38.9°C and a large discontinuous decrease occurs at this temperature. Above this transition point, T_c, the Curie-Weiss law, $\epsilon = C/(T-T_0)$, is satisfied, and a plot of the reciprocal dielectric constant versus temperature is a straight line, as seen in the figure, with $T_0 = -58$°C and $C = 3.2\times10^4$°C. The (001) plate has a low dielectric constant varying gradually from 20 at room temperature to 5 at liquid-nitrogen temperature without any anomaly. The (100) plate gave a small discontinuity at T_c as shown in Fig. 1. This might be attributed to a small component of the large anomaly in the [010] direction owing to the cutting error of the crystal plate, in contrast to the perfect orientation of the (001), "as-grown" crystal plate. This high anisotropy can be expected from the predominantly layer structure of this crystal. After most of this work was