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Ultrasonic Measurements in Single-Crystal Nb_3Sn

K. R. KELLER* AND J. J. HANAK
RCA Laboratories, Princeton, New Jersey

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Ultrasonic-velocity and attenuation measurements in Nb_3Sn indicate anomalous temperature dependences of the elastic moduli and sound absorption. At room temperature, the elastic moduli and the attenuation of 555-Mc/sec compressional waves are typical of those found for metals. The room-temperature elastic moduli have been determined as $C_{11}=2.538$, $C_{12}=1.124$, and $C_{44}=0.3957$ in units of 10^{12} dyn/cm^2. At 4.2°K, C_{11} and C_{44} are reduced by 35.1% and 32.8%, respectively, while C_{12} is increased by 46.4%. At 32°K, and at the superconducting-transition temperature, there are peaks in the attenuation-temperature curve. Below 18°K, the attenuation is temperature-independent.

INTRODUCTION

RECENTLY reported work on single-crystal[1] V_3Si describes anomalous changes in the elastic moduli and sound absorption upon cooling to low temperatures. Unlike the elastic moduli of most metals, those of V_3Si exhibit large temperature dependences. Indeed, $C_{11}-C_{12}$ approaches zero at a temperature of 22°K. Furthermore, the acoustic attenuation in V_3Si exhibits an anomalous temperature dependence above the superconducting transition temperature T_c, and does not follow the exponential behavior predicted by the BCS theory in the superconducting state.[2] At temperatures close to where $C_{11}-C_{12}$ approaches zero, some specimens of V_3Si have been observed to undergo a crystallographic phase transformation.[3]

Nb_3Sn, like V_3Si, is a β-tungsten (A-15 structure), high T_c superconductor, and therefore might be expected to have properties similar to those of V_3Si.[4] However, unlike V_3Si, satisfactory single-crystal specimens of Nb_3Sn are difficult to obtain. In order to investigate the elastic properties and the ultrasonic attenuation, a single crystal of Nb_3Sn was prepared by a novel technique, and the temperature dependence of the sound velocity and ultrasonic attenuation was measured. Preliminary results have been published[5]; the present paper gives more detail. The results obtained for Nb_3Sn are quite similar to those found for V_3Si, and suggest that the anomalous elastic properties are characteristic of high T_c, β-tungsten superconductors.

EXPERIMENTAL PROCEDURE

The Nb_3Sn single crystal which was measured was grown by the transport of HCl gas.[6] The chemical composition was 75.5±0.5 at.% niobium, with the remainder being tin. Mass spectrographic analysis indicated that the total impurity content (except hydrogen) was less than 100 ppm, of which the major impurities were: Fe, 40 ppm; O, 23 ppm; Si, 11 ppm; and Cr, 5.4 ppm. The dislocation density, determined from chemical-etch pits, was 1×10^4 cm^{-2}. The lattice constant was 5.295 Å, which is higher than the value of 5.290 Å reported[7] for stoichiometric Nb_3Sn. The corresponding theoretical density is 8.86 g cm^{-3}, which compares well with the value of 8.83 g cm^{-3} found for this crystal. The finished crystal weighted 0.883 g. The measured resistivity at 300°K was 11×10^{-5} Ω cm. The resistivity ratio was measured as $\rho(300°\text{K})/\rho(20°\text{K})\cong8$. The transition temperature, measured by an inductance method, was 18.1°K. In preparation for the ultrasonic measurements, it was polished on two (110) planes parallel to within 4±2 sec and flat to within $(1/15)\lambda$.

Ultrasonic-velocity and attenuation measurements were made on the sample crystal for wave propagation in the [110] direction ($\mathbf{q}_c \| [110]$). Sound waves were generated by X-cut and Y-cut quartz transducers which were bonded to the Nb_3Sn crystal with GE varnish or Dow-Corning DC-200 oil of 1000-centistokes viscosity. Two different bonding materials were used in order to verify that the choice of material did not alter the measured quantities.

Velocity measurements were made using 42-Mc/sec and 21-Mc/sec sound waves. The velocity was determined by measurement of the elapsed time between echos with a calibrated delay circuit, resulting in an estimated accuracy of ±0.1% in the velocity. These data are uncorrected for thermal expansion. Attenuation measurements were made over a limited temperature range for 555-Mc/sec compressional waves, and for shear waves with [001] polarization ($\xi \| [001]$), by the pulse-echo technique, with an estimated accuracy of ±0.2 dB/cm.

Elastic Properties

In Fig. 1, the temperature dependence of the compression-wave velocity v_c is shown for wave-propagation vector $\mathbf{q}_c$, in the [110] direction. Figures 2 and 3 show

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* Present address: RCA EC&D, Somerville, New Jersey.

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

[2] J. Bardeen and J. R. Schrieffer, *Progress in Low Temperature Physics* (North-Holland Publishing Company, Amsterdam, 1961), Vol. 3, p. 216.

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

[4] L. R. Testardi has made velocity measurements on polycrystalline Nb_3Sn, Nb_3Al, and V_3Ga which indicate that these materials also have anomalous elastic behavior (private communication).

[5] K. R. Keller and J. J. Hanak, Phys. Letters **21**, 263 (1966).

[6] J. J. Hanak and H. S. Berman, in *Proceedings of the International Conference on Crystal Growth, Boston, Massachusetts, 1966*, edited by H. Steffen Peiser (Pergamon Press, New York, 1967), p. 249.

[7] J. J. Hanak, K. Strater, and G. W. Cullen, RCA Rev. **25**, 342 (1964).

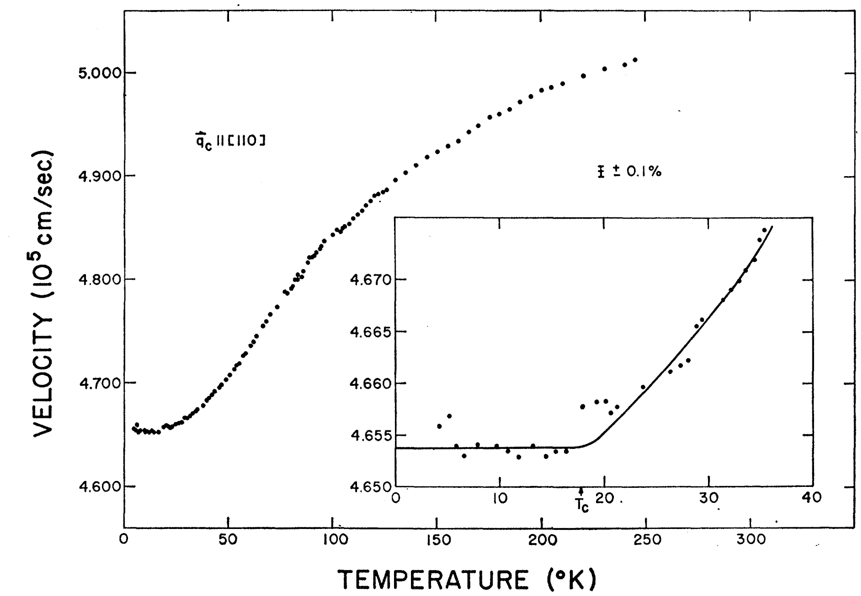

FIG. 1. The velocity as a function of temperature of compressional sound waves propagated in the [110] direction in Nb_3Sn. The inset shows an expanded plot of the low-temperature region.

the sound velocities for shear waves with $\mathbf{q}_s\|[110]$ and particle motion $\xi\|[001]$ and $\xi\|[\bar{1}10]$, respectively, where ξ is the polarization vector. The velocities are tabulated for several temperatures in Table I. At room temperature, the sound velocities are typical of those for solids. However, as the temperature is decreased, the velocities of all three modes show large decreases. T_c marks the arrest of velocity change for compressional waves, while for shear waves with $\xi\|[001]$, the change continues down to 4°K. However, the rate of change is altered at 32°K, which is near the temperature T_m, where a crystallographic-phase transformation, similar to that observed in V_3Si, is believed to take place[3] in Nb_3Sn. Even more striking is the shear wave with $\xi\|[\bar{1}10]$. Below 32°K, this mode could not be propagated. In order to verify that the loss of this shear mode is a property of the Nb_3Sn and not the experimental technique, a 21-Mc/sec transducer was bonded to the crystal so that ξ was 45° to the [001] and [$\bar{1}$10] directions. In this way, both shear modes were generated simultaneously. The two shear velocities are sufficiently different at low temperatures so that the two sets of echos did not overlap for the duration of several echos. As the temperature was lowered below 35°K, the attenuation of the mode with $\xi\|[\bar{1}10]$ increased very rapidly. Below 32°K, this mode had completely disappeared while the mode with $\xi\|[001]$ remained. Therefore, it was concluded that the loss of sound was a property of the sample and not an experimental effect.

The elastic moduli for single-crystal Nb_3Sn were computed by reading the velocity values from smooth curves drawn on the velocity-temperature plots. Below 32°K, the shear wave with the modulus $C_{11}-C_{12}/2$ ($\xi\|[\bar{1}10]$) could not be propagated. Therefore, C_{11} was taken equal to C_{12} below 32°K. The resulting curves are shown in Fig. 4. In Table II, the elastic moduli for Nb_3Sn are shown at 300, 35, and 0°K. The 300 and 0°K moduli for V_3Si, computed from the data in Ref. 1, and the corresponding values for Al are shown for comparison.[8] The moduli C_{11} and C_{12} and change in moduli are similar for the β-tungsten-structure superconductors, while C_{44} and ΔC_{44} differ considerably. In the case of Al,

TABLE I. Sound velocities in Nb_3Sn in units of 10^5 cm sec^{-1} for propagation in the [110] direction.

Mode	Temperature (°K)	Velocity
Compressional $\xi\|[110]$	300 35 4.2	5.022 4.674 4.654
Shear $\xi\|[001]$	300 35 4.2	2.117 1.748 1.737
Shear $\xi\|[\bar{1}10]$	300 35 4.2	2.830 0.496 ...

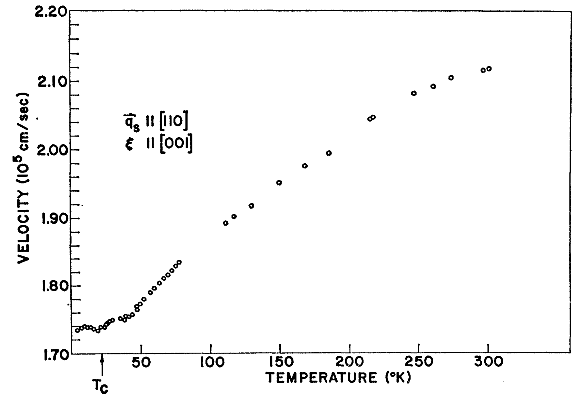

FIG. 2. The velocity as a function of temperature of shear sound waves polarized [001], propagated in the [110] direction in Nb_3Sn.

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[8] G. N. Kamm and G. A. Alers, J. Appl. Phys. 35, 327 (1964).

TABLE II. Elastic moduli[a] for Nb_3Sn, V_3Si, and Al in units of 10^{11} dyn/cm^2.

	Temperature (°K)	Nb_3Sn	V_3Si	Al
C_{11}	300	25.38	28.70	10.68
	35	16.79	...	...
	0	16.46	17.97	11.43
$\Delta C_{11}/C_{11}(300)$[b]		−35.1%	−37.4%	+7.0%
C_{12}	300	11.24	12.02	6.074
	35	16.37	...	...
	0	16.46	17.97	6.192
$\Delta C_{12}/C_{12}(300)$		+46.4%	+49.5%	+1.9%
C_{44}	300	3.960	8.096	2.821
	35	2.698	...	...
	0	2.663	7.626	3.162
$\Delta C_{44}/C_{44}(300)$		−32.8%	−5.8%	+12.1%

[a] The elastic moduli for V_3Si are taken from the data given in Ref. 1. The elastic constants for Al are taken from Ref. 8.

[b] $\Delta C = C_{(0)} - C_{(300)}$.

which is taken as representative of metals, the lattice stiffens upon cooling, while the β-tungsten superconductors soften. The softening can be described by the stiffness parameter $S = (C_{11} - C_{12})/2C_{44}$, which is unity for an isotropic material. The temperature dependence of S for Nb_3Sn, and that of V_3Si and Al, for comparison, is shown in Fig. 5.

At room temperature, the value $S = 1.78$ for Nb_3Sn is typical of metals[9] having cubic-crystal structure. As the temperature is lowered to 35°K, S decreases by a factor of ~20 below its room-temperature value. The rate of decrease is such that by linear extrapolation, S would go to zero at 32°K, which is close to the value of T_m reported[3] for Nb_3Sn. The observed decrease in S is taken as indirect evidence that the Nb_3Sn crystal which was measured does experience a crystallographic-phase transformation. There is at present no direct evidence that a phase change occurs.

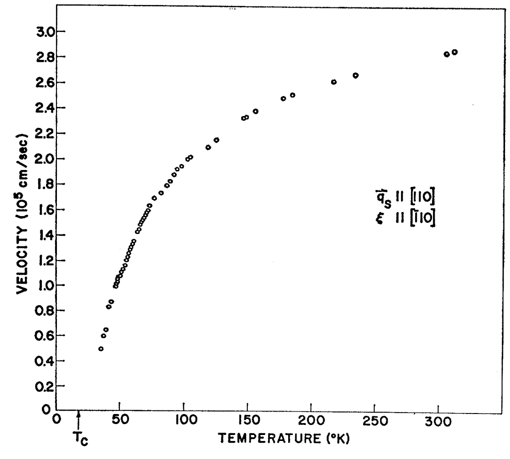

FIG. 3. The velocity as a function of temperature of shear sound waves polarized $[\bar{1}10]$, propagated in the $[110]$ direction. Below 35°K, this mode could not be propagated.

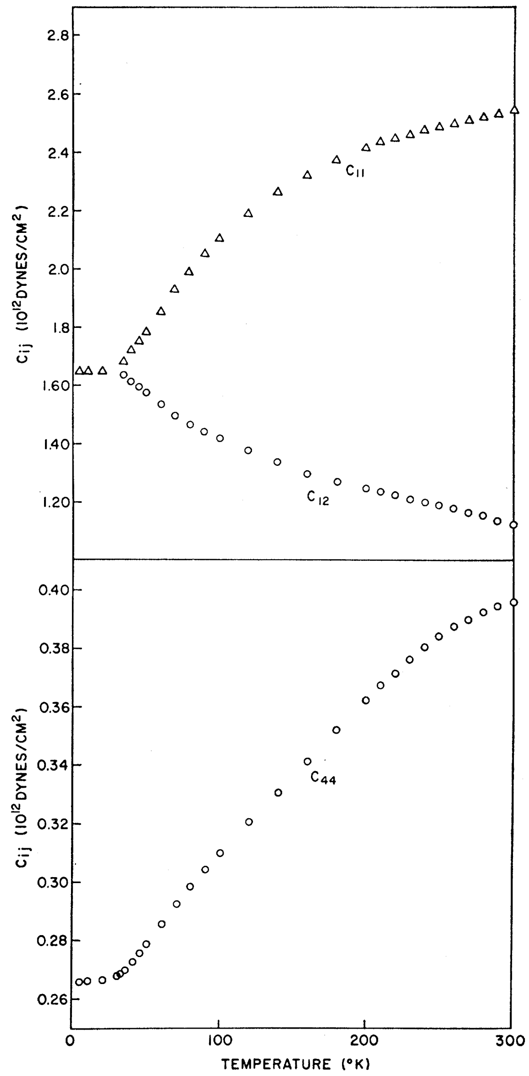

FIG. 4. The computed elastic moduli of Nb_3Sn as a function of temperature (note the change of ordinate).

An important parameter used to describe the transport properties of solids is the Debye temperature, which may be calculated from the low-temperature limit of the elastic moduli. Since the elastic moduli of Nb_3Sn vary appreciably with temperature, it is interesting to calculate a characteristic temperature $\Theta^*(T)$, which may be interpreted in terms of a mean-lattice-vibrational frequency. The low-temperature limit of $\Theta^*(T)$ is then the Debye temperature. $\Theta^*(T)$, shown in Fig. 6, was calculated over the range from 4.2 to 300°K, using the approximation of Anderson.[10] The temperature dependence of $\Theta^*(T)$ was fitted down to 40°K within 1% to the empirical relation

$$1/\Theta^* = 2.72 \times 10^{-3} + 0.110(1/T), \qquad (1)$$

which gives a high-temperature limit for $\Theta^*(T)$ of

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[9] M. Greenspan, in *American Institute of Physics Handbook*, edited by D. E. Gray (McGraw-Hill Book Company, Inc., New York, 1957), pp. 3-81.

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

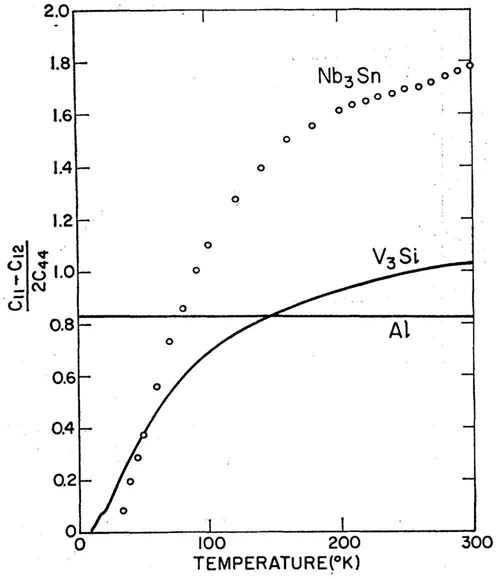

FIG. 5. The stiffness parameter $S=(C_{11}-C_{12})/2C_{44}$ as a function of temperature for Nb_3Sn, V_3Si, and Al. The data for V_3Si are from Ref. 1 and for Al from Ref. 8.

368°K. Equation (1) is not valid below 40°K; however, the calculated characteristic temperature approaches a low-temperature limit of 132°K. $\Theta^*(T)$ is not necessarily related to the Debye temperature found from specific-heat measurement, but it can be used for describing the resistivity data for Nb_3Sn of Woodard and Cody.[11] Their measured resistivity can be fitted from 300°K down to 40°K within 3% by the expression

$$1/\rho=1.24\times10^7[1/\Theta^*(T)]-2.60\times10^4$$

for their sample FS-20. Below 40°K, there appears to be no correlation between the resistivity and Θ^*.

As noted, the elastic properties of V_3Si and Nb_3Sn are similar. $\Theta^*(0)$ and $\Theta^*(300)$ were calculated for V_3Si from the elastic moduli, and it is interesting to note that

$$\frac{\Theta^*(0)[V_3Si]}{\Theta^*(0)[Nb_3Sn]}=\frac{\Theta^*(300)[V_3Si]}{\Theta^*(300)[Nb_3Sn]}=\left(\frac{M[Nb_3Sn]}{M[V_3Si]}\right)^{1/2}=1.5,$$

where M is the molecular weight. This relationship between Θ^* and M might be expected for a Debye solid. Furthermore,

$$T_m[Nb_3Sn]/T_m[V_3Si]=1.5$$

is again related to the square root of the mean masses.

Ultrasonic Attenuation

The ultrasonic attenuation for 555-Mc/sec waves as a function of temperature is shown in Fig. 7 for compressional waves. Upon cooling the sample, the attenuation reaches a maximum, and then decreases with further cooling. At T_c. a large peak in the attenuation is observed. Below T_c, the attenuation becomes temperature-independent.

The attenuation of compressional waves by electrons for $ql<1$, where l is the electronic mean free path, is given by Mason and Bommel[12] as

$$\alpha_c=\frac{2\omega^2\hbar^2\sigma(3\pi^2N)^{2/3}}{15\rho v_c^3e^2}, \qquad (2)$$

where ω is the sound frequency, v_c is the sound velocity, σ is the conductivity, N is the electron density, e is the electronic charge, and ρ is the density of the material. Substituting for Nb_3Sn, $N=2.55\times10^{23}$ electrons/cm^3 (valence of 4.75), and the measured values of σ, ρ, ω, and v_c give $\alpha_c=0.012$ dB/cm at 50°C, which is a factor of 500 smaller than the measured value. The temperature dependence of α_c in Eq. (2) is contained in σ and v_c. Substituting the measured $v_c(T)$ and $\sigma(T)$ given by Woodard and Cody[11] in Eq. (2) gives a temperature dependence which agrees with the experimental temperature dependence to within 20% down to 35°K. However, in view of the large discrepancy in the absolute value of the measured and calculated attenuation, this agreement is accidental.

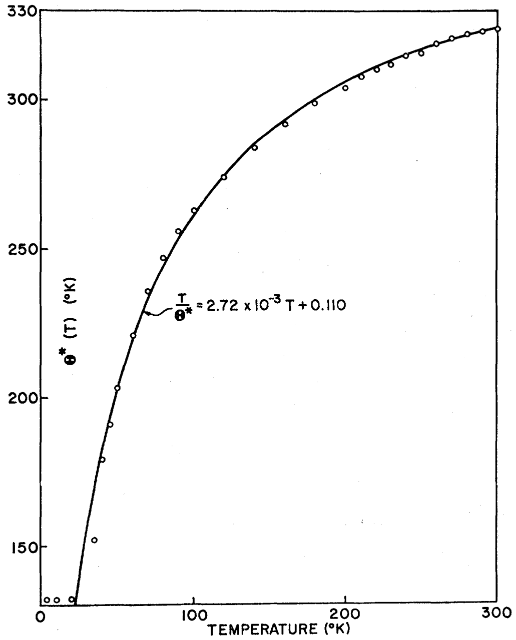

FIG. 6. The characteristic temperature $\theta^*(T)$ as computed from the elastic moduli.

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[11] D. Woodard and G. Cody, RCA Rev. **25**, 393 (1964); also Phys. Rev. **136**, A166 (1964). It is of interest to note that the slope of the resistivity curves shows a discontinuous increase of about 12% at 28°K for samples with $T_c\simeq18.3$°K, and at 32°K for samples with $T_c\simeq17$°K.

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

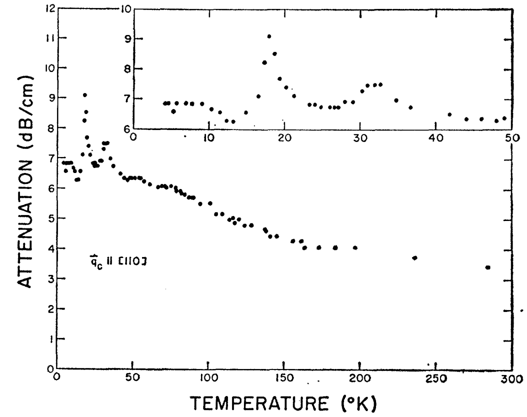

FIG. 7. The attenuation of 555-Mc/sec compressional waves propagated in [110] direction in Nb_3Sn.

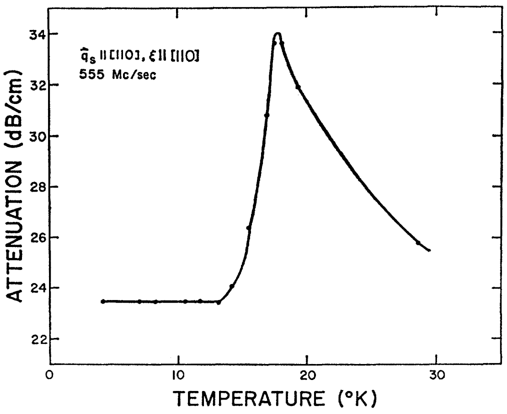

FIG. 8. The attenuation of 555-Mc/sec shear waves polarized [001], propagated in the [110] direction in Nb_3Sn.

Although there is no direct evidence as yet, one can speculate that for this specimen of Nb_3Sn, a crystallographic-phase transformation is taking place, with T_m marking the onset of the transformation, and T_c its termination. A possible explanation for the variation of α_c in this interval would then be that the sound is scattered by tetragonal domains of Nb_3Sn. The domains can change orientation as temperature is changed,[13] and hence alter the scattering of sound with changing temperature.

At temperatures lower than T_c, α_c does not show an exponential temperature dependence as expected for the superconducting state. In Pb, a departure from an exponential decrease in α_c below T_c has been observed.[12,14] Here, α_c is dependent on the acoustic power, which is attributed to the unpinning of line dislocations.[15] In Nb_3Sn, α_c is independent of acoustic power up to the highest power available for these measurements (100-mW acoustic power). If $\Theta^*(0)$ is taken as the Debye temperature, the high value of $T_c/\Theta^*(0)$ $(=0.17)$ indicates that electron-phonon coupling is considerably greater than in most superconductors, and thus Nb_3Sn may not show the variation of α_c with temperature predicted by the BCS theory.

The attenuation for 555-Mc/sec shear waves, α_s, is shown in Fig. 8. α_s also shows a peak at T_c, and then becomes constant for lower temperatures. Unfortunately, the attenuation was not measured above 29°K. The ratio of α_s and α_c should be[12]

$$\alpha_s/\alpha_c = \tfrac{3}{4}(v_c/v_s)^3 \qquad (3)$$

at 29°K $(\alpha_s/\alpha_c)=3.8$, while $\tfrac{3}{4}(v_c/v_s)^3=13$. However, it is not clear that Eq. (3) should be valid, since it is not certain what mechanism is involved in the attenuation of sound.

CONCLUSION

Nb_3Sn, like V_3Si, experiences a softening of the lattice as temperature is reduced. The degree of softening is sufficiently great to prohibit the propagation of one shear mode below the temperature at which a crystallographic-phase transformation may take place. The temperature dependence of the ultrasonic attenuation of compressional waves is much weaker than that observed for pure metals. Moreover, in the superconducting state, the temperature dependence of the attenuation does not agree with the BCS predictions, but this may be due to strong coupling effects. The present results suggest that the anomalous resistivity observed previously is related to the anomalous temperature dependence of the elastic moduli. Finally, the computed Debye temperatures for V_3Si and Nb_3Sn scale as the square root of the masses, as do the extrapolated temperatures T_m.

ACKNOWLEDGMENTS

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[13] B. W. Batterman (private communication).

[14] R. E. Love and R. W. Shaw, Rev. Mod. Phys. 136, 260 (1964).

[15] B. R. Tittman and H. E. Bommel, Phys. Rev. Letters 14, 296 (1965).