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Shear-mode anomaly, precursor effects, and pressure dependence of the structural phase transformation in Nb_3Sn

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A spread-out discontinuity in the shear modulus c_{44} has been observed ultrasonically at the structural transformation in Nb_3Sn near 45 K and explained in terms of static anharmonic coupling of the shear strain η_{23} to the tetragonal transformation strain. Transformation precursors in c_{44} begin to appear a few degrees above the transformation temperature and are correlated with precursor behavior in the soft shear modulus $(c_{11}\text{-}c_{12})/2$ and also observed with x rays. The pressure coefficient of the transformation temperature determined from the pressure-induced shift of the discontinuity in c_{44} is in good agreement with an earlier measurement by Chu. Some evidence for the possible existence of a tricritical point near 0.7 GPa is presented.

I. INTRODUCTION

Nb_3Sn undergoes a ferroelastic weakly first-order phase transformation near 45 K from the cubic $A15$ structure (O_h^3) to a tetragonal low-temperature structure (D_{4h}^9).[1-5] This transformation has also been observed in other $A15$ compounds[6] and is for Nb_3Sn and V_3Si known to be associated with a softening of the shear modulus $c_s = (c_{11}\text{-}c_{12})/2$, but the mode softening occurs also in nontransforming samples.[6-8] The transformation and the mode softening are of particular interest because they are associated with large anharmonicity, magnetic-property anomalies, and high superconducting transition temperatures.[6] Moreover, conspicuous dynamic phenomena, consisting of a large difference between the phonon velocities in the collision-dominated and the ballistic regimes, and of a central peak in neutron scattering measurements have been observed above the structural transformation temperature T_L (Ref. 9). Transformation precursor effects above T_L have been observed for V_3Si and Nb_3Sn in thermal expansion[10-12] and studied by means of x ray and neutron scattering experiments,[13] but their relation to and the nature of the pretransformation instabilities invoked by Varma, Phillips, and Chui[14] and Phillips[15] for explaining the kink in the (110) TA_1-phonon dispersion curve[9] is still not understood.

The purpose of the present paper is to report an ultrasonic anomaly Δc_{44} of the shear modulus c_{44} for Nb_3Sn as a function of temperature and pressure in the vicinity of T_L, which consists of a smeared-out discontinuity and reveals transformation precursor effects. The anomaly Δc_{44} appears to be a static feature and is attributed to anharmonic coupling of the shear strain η_{23} to the tetragonal transformation strain. The precursor effects in Δc_{44} are correlated with the temperature shift between the directly and indirectly measured shear modulus c_s and with the d-spacing fluctuations observed with x rays,[3] which for V_3Si have been shown to be greatly enhanced near the crystal surface.[13] The pressure coefficient $(\partial T_L/\partial p)$ determined from the pressure-induced shift of Δc_{44} in temperature is in good agreement with the initial slope below 0.7 GPa measured by Chu.[16] On the other hand, the pressure coefficient measured by Chu[16] above 0.7 GPa agrees well with the value determined by the stability limit $c_s(p,T) = 0$ of the soft shear modulus.[17] This suggests the possibility that the discontinuity in the slope $(\partial T_L/\partial p)$ at about 0.7 GPa could represent a tricritical point.[18]

II. EXPERIMENTAL DETAILS

A platelet with a pair of parallel (110) faces 1.926 mm apart and with lateral dimensions of about 3 to 4 mm was prepared from a single crystal of Nb_3Sn which had been grown by an HCl-gas-transport method[19] and subsequently annealed in vacuum for about 50 h at 1000 °C. The crystal undergoes the structural transformation at about 45 K and was used previously for measuring the pressure dependence of the elastic constants.[17] An ac cut quartz transducer of 3.1-mm diameter was glued to one of the (110) faces by means of Nonaq transducer stopcock grease, and the round-trip delay time of 20-MHz transverse waves, polarized in [001], was measured as a function of temperature and pressure by means of the pulse superposition method.[20] Helium gas was used as pressure medium. The temperature was controlled and measured with a precision of better than 0.01 K and with an absolute accuracy of better than 0.2 K. The accuracy of the pressure measurement

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was about 0.3 MPa. Details of the experimental design have been given before.[17,21]

The measurements were made as a function of temperature from about 40 to 50 K for five constant values of pressure in the order of decreasing pressure, starting with a value of 0.136 GPa. Since the sample-transducer bond deteriorates as the external pressure is completely removed no measurements were made at ambient pressure. However, from the known pressures dependence of the elastic constants[17] it follows that for practical purposes the data at the lowest pressure used of 0.011 GPa may also be considered as pertaining to atmospheric pressure.

Since the temperature runs were made with the pressure valves closed, thus representing constant volume, between 40 and 50 K the pressure actually changed at a rate of less than 0.3 MPa/K. The pressure values quoted represent the actual pressure at the structural transformation temperature for a given run.

III. EXPERIMENTAL RESULTS AND INTERPRETATION

A. Shear modulus c_{44}

In Fig. 1 the temperature dependence of the shear modulus c_{44} at 0.011 GPa as determined from the transit time of the [110],[001] mode is plotted in the vicinity of the structural transformation. In the tetragonal phase these data are domain averages. For comparison, two sets of data for the shear modulus c_s at atmospheric pressure are also plotted and will be discussed below.

For c_{44} three regions consisting of the tetragonal region below the step, the intermediate region including the step, and the cubic region above the step may be discerned. Hysteresis is observed in the tetragonal region and the intermediate region and amounts to up to 1 and 0.5 K, respectively. In the tetragonal region it is attributed to domain reorientation, in the intermediate region to superheating and supercooling effects associated with nucleation phenomena typical for a first-order phase transition. About 7 K below the center of the step the hysteresis effects disappear, apparently so because of a stable domain configuration. The intermediate region is interpreted as the two-phase region of a first-order phase transition which is spread out because of crystal inhomogeneities and/or because of stabilization of the cubic phase resulting from the internal stresses, induced by nuclei of the tetragonal phase. The transition from the cubic to the intermediate region is gradual, with transformation precursors being apparent.

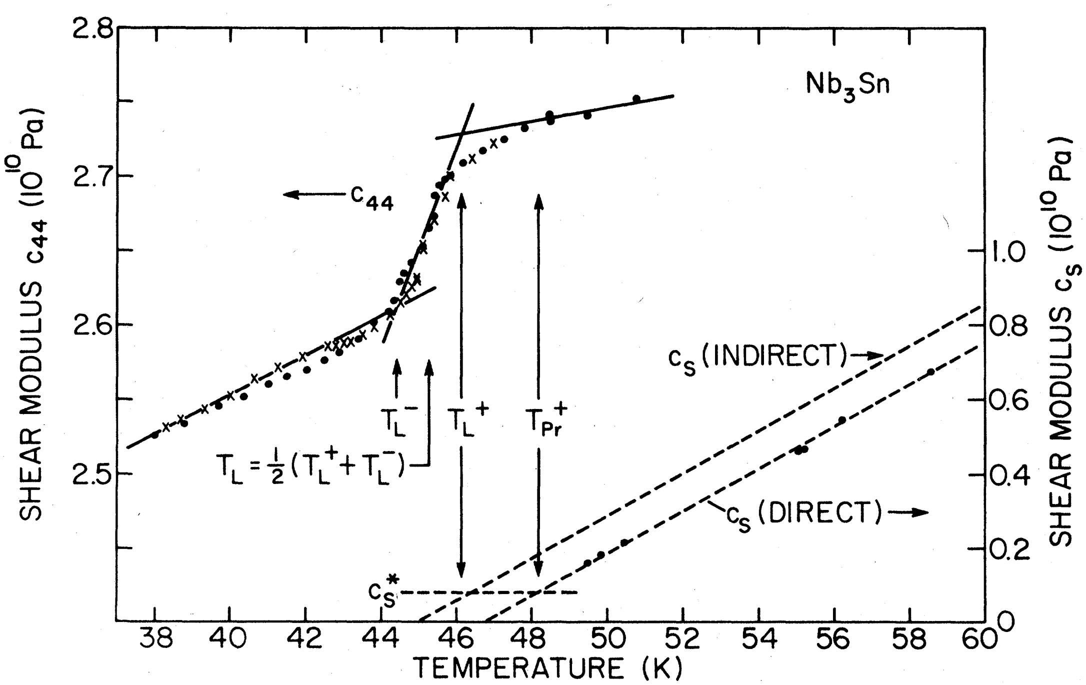

FIG. 1. Temperature variation of the shear moduli c_{44} and c_s near the structural transformation from the two shear modes propagating in [110]. For c_{44} the data were taken at 0.011 GPa, and the circles and crosses refer to decreasing and increasing temperature, respectively. Following Vieland *et al.* (Ref. 3) c_s(indirect) was calculated from the velocity of the longitudinal mode in [110], from c_{44} and from the observation of a temperature-independent bulk modulus $B = 1.712 \times 10^{11}$ Pa below 100 K (Ref. 17).

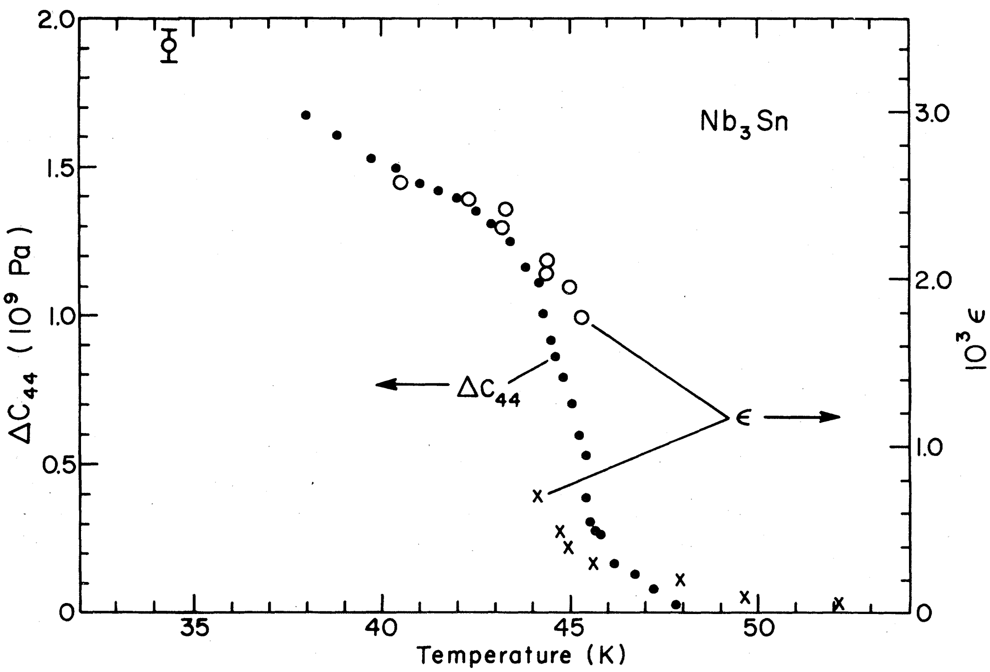

FIG. 2. Comparison of the shear-modulus decrement Δc_{44} (filled circles) associated with the structural transformation with the transformation strain ϵ determined with x rays (Ref. 3). Crosses and open circles denote the shift in the high-T peaks and the tetragonality of the wing (domain) peaks, respectively (Ref. 3).

By linear extrapolation of the data from the hysteresis-free section of the tetragonal regime, from the inflection point in the intermediate region, and from the region above the precursor region of the cubic region three tangents with the intercepts denoted by T_L^+ and T_L^- are obtained. The transition temperature is taken to be $T_L = (T_L^+ + T_L^-)/2 = 45.25$ K, and the width of the intermediate region is given by $T_L^+ - T_L^- = 1.7$ K. The onset of transformation precursors in the cubic region is denoted by the temperature T_{pr}^+.

Figure 2 shows the shear-modulus decrement $\Delta c_{44} = c_{44}^{\mathrm{cub}} - c_{44}$ vs T (filled circles), with c_{44}^{cub} tangentially extrapolated from the region $T > T_{\mathrm{pr}}^+$. For comparison, the tetragonal transformation strain ϵ, defined in terms of the lattice parameters a and c in the tetragonal phase according to

$$\epsilon = \tfrac{2}{3}(1 - c/a) \tag{1}$$

and determined by x rays on a similar sample[3] is also plotted in Fig. 2. The two types of data shown were obtained from line shifts of the x-ray peaks above and from additional sidepeaks occurring below T_L as a result of tetragonal domains (open circles). It is apparent that for $T \lesssim T_L^- = 44.4$K Δc_{44} is approximately proportional to ϵ.

$$\Delta c_{44} = A\,\epsilon \ . \tag{2}$$

For the proportionality constant a value of $A = 5.6 \times 10^{11}$ Pa is found. For $T \gtrsim T_L^+ = 46.1$ K the magnitude of the precursor discernible in Δc_{44} is also roughly proportional to ϵ, with the same average proportionality constant A. However, the x-ray precursor strain extends over a larger temperature interval, most likely so because of sample differences. These relations between Δc_{44} and ϵ suggest that the decrement Δc_{44} is a static feature, caused by anharmonic coupling of the shear strain η_{23} to the tetragonal transformation strain ϵ, and that the precursors in Δc_{44} and ϵ have a common microscopic origin.

B. Anharmonic coupling

Acoustic anomalies, usually consisting of steps and/or cusps in the temperature variation of the elastic constants are a common feature of structural phase transformations and may arise from static or dynamic coupling of the elastic strain to the transformation coordinate (order parameter).[22–24] A phenomenological description of these effects may be given on the basis of the Landau theory of second-order phase transitions[25] even in the case of weakly first-order transitions. In the most elaborate of the Landau theories for the $A15$ compounds the elastic strains are coupled via the Γ_{12} optic-phonon modes to d-electron charge-density-wave (CDW) amplitudes of the transition-metal chains.[26] However, the CDW model, or equivalently the Peierls instability model of Gor'kov[27] is not substantiated by frozen phonon calculations for Nb_3Ge.[28] Other possible primary order parameters are the Jahn-Teller band splittings at the R point,[29] possibly in conjunction with the Γ point[30] or other high-symmetry points.[28,31] Common to these theories is a linear coupling of the primary electronic order parameter to the tetragonal transformation strain, so that in the vicinity of the transformation the distinction between the two becomes immaterial to lowest order in the temperature variation. Therefore, most of the acoustic anomaly in c_{44} is attributed to direct anharmonic coupling of the [110],[001] shear strain to the tetragonal transformation strain, which is considered as the primary order parameter. Other coupling effects neglected are of higher order.

The relevant lowest-order coupling term in the Landau free energy per unit initial volume V_0 is for O_h symmetry given by[32]

$$\frac{\Delta F}{V_0}=\frac{1}{2}\,\hat{c}_{244}\left[e_2(e_4^2-e_5^2)+\frac{1}{\sqrt{3}}e_3(e_4^2+e_5^2-2e_6^2)\right] . \tag{3}$$

Here

$$\begin{aligned} &e_1=(\eta_1+\eta_2+\eta_3)/\sqrt{3},\quad e_2=(\eta_1-\eta_2)/\sqrt{2},\\ &e_3=(\eta_1+\eta_2-2\eta_3)/\sqrt{6},\quad e_4=\eta_4,\\ &e_5=\eta_5,\quad e_6=\eta_6 \end{aligned} \tag{4}$$

are the symmetry coordinates of the Lagrangian strain tensor with components η_μ ($\mu=1,2,\ldots,6$) in Voigt notation, appropriate for cubic symmetry.[24] The third-order elastic (TOE) constant $\hat{c}_{244}$, referred to symmetry coordinates, is related to the TOE constants $c_{\mu\nu\lambda}$ in Voigt notation according to Brugger's definition[33] by

$$\hat{c}_{244}=(c_{144}-c_{166})/\sqrt{2} . \tag{5}$$

For the cubic point group O_h the sets of symmetry coordinates e_1; (e_2,e_3); (e_4,e_5,e_6) form basis functions to the irreducible representations $\Gamma_1,\Gamma_{12},\Gamma_{25}'$, respectively.[24] For a Cartesian coordinate system coinciding with the three cubic axes the transformation strain for a single-domain crystal with its tetragonal axis in the x_3 direction is given by $\eta_{11}=\eta_{22}=-\eta_{33}/2=\epsilon/2$, or $e_1=e_2=0$, $e_3=\sqrt{3/2}\epsilon$. Since the transition does not involve a volume change[3] the strain parameter ϵ is to lowest order in the change of the lattice constant given by Eq. (1). Noting that the elastic constant for a [110],[001] shear strain is identical to that for a [010],[001] shear strain, which is described by $e_4=\eta_4$, one obtains the contribution Δc_{44} to the associated shear modulus arising from the static anharmonic coupling to the tetragonal transformation strain by differentiating Eq. (3) with respect to e_4 and using Eq. (5) as

$$\Delta c_{44}=(c_{144}-c_{166})(\epsilon/2) . \tag{6}$$

This formula is only approximately correct, because the derivation given here is based on the implicit assumption of additivity of the strains e_3 and e_4. The correct formula is derived on the Appendix by using the formalism of nonlinear elasticity theory for the propagation of ultrasonic waves in homogeneously strained crystals.[34] Considering a multidomain crystal and assuming additivity for the contributions of the individual domains with their tetragonal axes along any of the cubic axes of the prototype phase one obtains for the shear-modulus decrement corresponding to the [110],[001] shear mode:

$$\Delta c_{44}=(3f-1)(4c_{44}+c_{166}-c_{144})(\epsilon/4) . \tag{7}$$

Here f denotes the volume fraction of the domains with tetragonal axis in [001]. For $f=1$ Eq. (7) reduces to the corrected form of Eq. (6), with a term $4c_{44}$ added to the TOE constants. According to Eq. (7) for random domain distribution ($f=\frac{1}{3}$) the shear-modulus decrement is zero.

Since the domain configuration is unknown it is not possible to determine the TOE constants from the constant A defined above. However, the TOE constants c_{111},c_{112},c_{123} have been determined semiempirically from experimental elastic and x ray data on the basis of a Landau model.[35] By assuming the Cauchy relations $c_{112}=c_{166}$ and $c_{123}=c_{144}$ one obtains from these values after extrapolation to 45 K the difference $c_{166}-c_{144}=-9.5\times10^{12}$ Pa. In conjunction with the above value of A an estimate of $f=0.25$ is obtained from Eq. (7), i.e., the shear-modulus decrement could be caused by a rather small preferential alignment of the domains perpendicular to [001], as may perhaps be caused by the stress exerted by the quartz transducer at the pressure of 0.011 GPa. On the other hand, for perfect alignment in [001] a considerably larger and negative value of A and consequently a shear-modulus decrement of opposite sign should result.

It is conceivable that the shear-modulus decrement includes contribution from other mechanisms, especially from domain-wall motion and domain reorientation. In order to substantiate the above interpretation and conclusions, additional studies are therefore required, such as ultrasonic attenuation measurements and ultrasonic velocity measurements on single domain crystals. For $SrTiO_3$, which undergoes a structural transformation near 105 K from cubic to tetragonal symmetry, it has been possible to eliminate domain effects on the elastic modulus decrements in ultrasonic measurements under biaxial compression.[36] For Nb_3Sn single domain crystals could be obtained by uniaxial compression, but unfortunately, the crystal available was too small for such measurements.

C. Precursor effects

It has been noted that for Nb_3Sn the directly measured soft shear modulus c_s extrapolates to zero several degrees above T_L and should be more representative of those regions in the crystal which are softened by inhomogeneities.[3] On the other hand, the shear modulus determined indirectly from the measured longitudinal modulus c_{11} and from the fact that below 100 K the bulk modulus $B=(c_{11}+2c_{12})/3$ is temperature independent, extrapolates to zero a few tenths of a degree below T_L, and should be more representative of the bulk of the crystal.[3] The temperature shift between c_s(direct) and c_s(indirect) was found to correlate approximately with the temperature range over which the precursor strain observed with x rays (crosses in Fig. 2) occurred.[3] Following this procedure two sets of data for the shear modulus c_s were calculated and are plotted in Fig. 1. They consist of c_s(direct), determined from the transit time of the [110],[1$\bar{1}$0] mode, and of c_s(indirect), calculated from the transit times of the other two pure modes in [110] [corresponding to the elastic constants $(c_{11}+c_{12})/2+c_{44}$ and c_{44}, respectively] and from the assumption of a temperature-independent bulk modulus $B=1.712\times10^{11}$ Pa (Ref. 17). It is apparent that at the temperature $T_{\rm pr}^+$, indicating the onset of precursors in c_{44} the directly measured shear modulus equals some value c_s^*, and that at the temperature T_L^+, indicating the onset of the bulk transformation, c_s(indirect) equals the same value c_s^*. Following Vieland *et al.*[3] the condition $c_s(T)=c_s^*$ is interpreted as the vanishing of the Landau free energy, which defines T_L. Consequently, $T_{\rm pr}^+$ and T_L^+ defined in terms of $c_s(\text{direct})=c_s^*$ and $c_s(\text{indirect})=c_s^*$ represent the upper bounds for T_L pertaining to the soft precursor regions and to the bulk of the crystal, respectively. For the sample studied by Vieland *et al.*[3] the temperature range $T_{\rm pr}^+-T_L^+$ over which precursors were observed both with x rays[3] and in the shear modulus c_s (Ref. 8) amounts to about 6 K, whereas for the present sample the precursor range apparent in c_{44} and c_s is only 2 K, perhaps because of higher sample homogeneity. Allowing for the effect of sample differences it may be concluded that the precursors apparent in the directly measured shear modulus c_{44}, in the difference between c_s(indirect) and c_s(direct), and in the line shifts of the x ray peaks in the cubic phase[3] are of common origin and indicate tetragonal regions above T_L.

By comparing x ray and neutron scattering linewidth data measured for V_3Si above T_L Hastings *et al.*[13] find *d*-spacing fluctuations which are enhanced near a free surface and which are attributed to microdomains of tetragonal symmetry. Tentatively the transformation precursors observed ultrasonically for Nb_3Sn may be identified with the surface-enhanced tetragonal microdomains in V_3Si. However, it should be noted that in V_3Si the transformation precursors have been observed at temperatures as high as 40 K above T_L, whereas in Nb_3Sn the precursors appear only a few degrees above T_L. The structural characteristics of the precursors and their relation to the microdomains proposed by Varma, Phillips, and Chui[14] and Phillips[15] for explaining the kink in the phonon dispersion curve[9] remain an open question.

D. Effect of pressure

The ultrasonic anomaly near the structural transformation was studied as a function of temperature at five different constant values of pressure (11, 38, 65, 107, and 136 MPa). In Fig. 3 the temperature dependence of the directly measured transit time of the [110],[001] shear mode is plotted for constant values of pressure. The three effects that may be inferred from these data are (i) an approximately quadratic increase of the area S under the hysteresis curve in the tetragonal region of the form $S=S_0(1+73p^2)$, where S_0 denotes the area at $p=0$ and p is in GPa, (ii) a linear decrease of the shear-modulus difference $\delta c_{44}=c_{44}^{\rm cub}-c_{44}^{\rm tetr}$ at $T=T_L$, where $c_{44}^{\rm cub}$ and $c_{44}^{\rm tetr}$ denote the values tangentially extrapolated from the cubic and from the hysteresis-free tetragonal regions, respectively, of the form $\delta c_{44}=1.02-2.5p$ (δc_{44} and p in GPa), and (iii) a linear increase of the transformation temperature as defined in Fig. 1 with pressure given by $T_L=45.21+2.8p$ (T_L in K, p in GPa).

The increase in the area S appears to indicate an increase in the activation energy for domain reorientation with pressure which is determined by the pressure dependence of the TOE constants and by the two domain configurations involved, neither one of which is independently known.

By definition, the shear-modulus difference δc_{44} represents the shear-modulus decrement for an ideally sharp first-order transition and in the absence of precursor effects. It is described by an expression similar to Eq. (7), but with ϵ denoting the spontaneous transformation strain at T_L for an ideal crystal. Thus the pressure dependence of δc_{44} arises from the effect of pressure on all three types of parameters in Eq. (7), viz., the volume fraction f of domains oriented in [001], the shear modulus c_{44} and the TOE constants c_{166} and c_{144}, and the spontaneous transformation strain ϵ. Again, these quantities are not independently known.

In Fig. 4 the transition temperature T_L as defined in Fig. 1 is plotted versus pressure. For comparison, the corresponding data of Chu[16] determined by measuring the pressure-induced shift of the inflection point in the temperature variation of the electrical

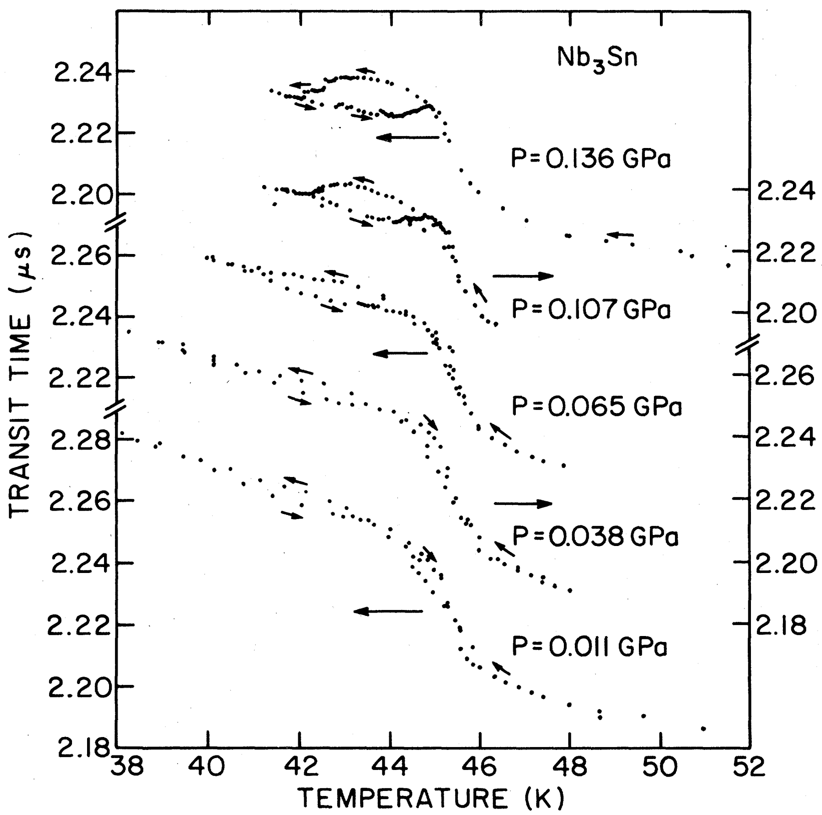

FIG. 3. Transit time of the shear mode propagating in [110], polarized in [001] vs temperature for five pressures.

resistivity over a larger pressure range are shown in the insert. It is apparent that the data of Chu show a discontinuity of slope at about 0.7 GPa, and that the initial slope below 0.7 GPa (2.9 K GPa^{-1}) agrees well with the slope from the pressure-induced shift of the shear-mode anomaly Δc_{44}, [(2.8 $\pm$0.1) K GPa^{-1}]. On the other hand, the pressure coefficient $(\partial T_L/\partial p)$ $=1.9$ K GPa^{-1} measured by Chu above 0.7 GPa is in good agreement with the value determined by the Born stability limit of the soft shear modulus, $c_s(p,T)=0$, for which the value $(\partial T_L/\partial p)=(2.0 \pm 0.4)$ K GPa^{-1} has been determined from the temperature and pressure derivatives of c_s (Ref. 17). This suggests that the discontinuity in the slope $(\partial T_L/\partial p)$ at about 0.7 GPa could represent a tricritical point[18] where the transition changes from first order below 0.7 GPa to second order above this pressure. In this case one would have to assume that below 0.7 GPa, T_L and the pressure coefficient $(\partial T_L/\partial p)$ are subject to systematic errors. These may arise, for example, from domain contributions or from the inhomogeneities and/or stresses responsible for the spreading of the transition over the temperature interval (T_L^-, T_L^+) (see Fig. 1).

The possible existence of a tricritical point is consistent with specific-heat data at high pressure which show a broadened cusp below 0.7 GPa and a step at and above this pressure.[16] The cusp could conceivably arise from a smeared-out latent heat, whereas the step might indicate a smeared-out λ-type anomaly. Furthermore, Chu notes that below 1 GPa the temperature coefficient of the resistivity exhibits a sharp peak near T_L, but that above 1 GPa only a broad hump is observed. This also could be related to the change in the order of the transition.

The pressure corresponding to the tricritical point is defined by the condition $c_s^*(p)=c_s(T_L(p),p)=0$, where, as stated above, the condition $c_s(T)=c_s^*$ defines the transition temperature T_L. By expanding $c_s(T,p)$ in powers of T and p up to second order and using the experimental values for the temperature and pressure derivatives of c_s (Ref. 17) and for $(\partial T_L/\partial p)$ a value for the tricritical pressure is obtained which is consistent with a value of 0.7 GPa, but because of the large experimental error of some of the (especially the second) derivatives this result is inconclusive.

On the other hand, semiempirical values of the third- and fourth-order elastic constants of Nb_3Sn (Ref. 35) imply an increase in the absolute magni-

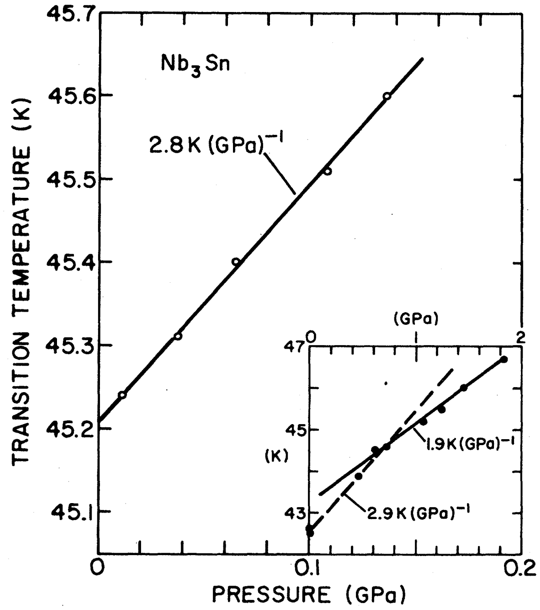

FIG. 4. Structural transformation temperature vs pressure. The insert shows the corresponding data of Chu (Ref. 16), linearly interpolated in the two regions below and above 0.7 GPa.

tude of the TOE constant $\hat{c}_{333}$ [referred to the symmetry coordinates, Eq. (4)] with increasing pressure and therefore rule out the existence of a tricritical point. In case these semiempirical data are experimentally confirmed the discontinuity in the slope (Fig. 4) could perhaps indicate a triple point.

The difference in the absolute values of the transition temperature at zero pressure as measured in the present study (45.2 K) and by Chu[16] (42.5 K) may be attributed to sample differences. The crystal studied by Chu[16] was part of a larger crystal, for which $T_L = 43$ K has been measured,[1(c)] and the value reported here agrees well with the value of 45 K measured on a similar crystal.[3] Thus for the present sample the tricritical point would be expected to occur at about 47 K and 0.7 GPa. Direct verification of the existence of the tricritical point is planned.

IV. SUMMARY AND CONCLUSIONS

An ultrasonic anomaly consisting of a spread-out discontinuity Δc_{44} of the shear modulus c_{44} and transformation precursors have been observed in Nb_3Sn near the structural transformation at about 45 K. The discontinuity Δc_{44} appears to be a static feature and may be attributed primarily to anharmonic coupling of the form $\eta_{23}^2\epsilon$ of the shear strain η_{23} to the tetragonal transformation strain ϵ, if it is assumed that the tetragonal domains are in part preferentially oriented. The anharmonic coupling parameter is consistent with available estimates for the pertinent third-order elastic constants. Transformation precursors apparent in c_{44} correlate with precursor effects in the soft shear modulus c_s and with x ray line shifts indicating tetragonal symmetry above the transformation temperature T_L, but their structural features and their effect on other properties, especially the kink in the [110] TA_1 phonon dispersion curve remain unknown.

The discontinuity Δc_{44} is sufficiently well defined so that its pressure-induced shift may be used to measure the pressure coefficient $(\partial T_L/\partial p)$. The result so obtained is in good agreement with the value obtained from resistance measurements.[16] A discontinuity in the pressure coefficient of T_L at about 0.7 GPa apparent in the resistance measurements[16] may indicate the existence of a tricritical point in Nb_3Sn, but a direct experimental verification remains the subject of further investigations.

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APPENDIX: CHANGE OF ELASTIC CONSTANTS AT A FERROELASTIC PHASE TRANSFORMATION

The purpose of this Appendix is to outline the derivation of a general expression for the change of the ultrasonically determined effective elastic constants occurring at a ferroelastic phase transformation, which is described by a one-parameter elastic transformation strain, and to apply this result to the derivation of Eq. (7) in the text. The method and nomenclature developed by Thurston and Brugger[34] for describing the velocity of small-amplitude elastic waves in homogeneously strained crystals will be used.

In the following, the natural and the initial state as introduced in Ref. 34 (denoted by a subscript 0 and by a tilde ~, respectively) are identified with the stress-free unstrained state of the high-symmetry prototype phase and with the stress-free state of the low-symmetry ferroelastic phase, respectively. The ferroelastic phase is characterized by the transformation strain $\tilde{\eta}_{ij}$ $(i,j = 1,2,3)$, referred to the high-symmetry prototype phase. Whereas in Ref. 34 the initial state emerges out of the natural state through application of an external stress, which produces an elastic strain, in the ferroelastic phase the stress tensor vanishes because of the equilibrium conditions.

The natural velocity W (defined as the total path length in the natural state, divided by the round-trip delay time of an elastic wave front in the initial state) is determined as the solution of a secular equation of the form (tensor notation) [cf. Eq. (3.14) of Ref. 34]:

$$\rho_0 W^2 U_j = w_{jk} U_k \quad . \tag{A1}$$

Here ρ_0 denotes the density in the natural state, and U_j are the components of the polarization vector of an elastic wave in the initial state, referred to the natural state. Furthermore [Eqs. (3.14) and (31.5) of Ref. 34] it is

$$w_{jk} = N_r N_s (\delta_{qk} + 2\tilde{\eta}_{qk}) \tilde{C}_{jrqs} \quad . \tag{A2}$$

Here N_r are the components of the unit vector normal to the wave front in the natural state. $\tilde{C}_{jrqs}$ is the adiabatic elastic constant tensor, evaluated in the initial state, which is expanded in powers of the transformation strain up to first order as

$$\tilde{C}_{jrqs} = C_{jrqs} + C_{jrqsmn} \tilde{\eta}_{mn} \quad . \tag{A3}$$

The constants on the right-hand side are the adiabatic second order, and the mixed adiabatic-isothermal third-order elastic constants in the natural state.

If the transformation strain may be represented in terms of a single parameter ϵ according to

$$\tilde{\eta}_{ij} = H_{ij} \epsilon \quad , \tag{A4}$$

where H_{ij} denotes numerical constants, the effective elastic constant increment $\Delta c = (\rho_0 \tilde{W}^2 - \rho_0 W_0^2)$ of the acoustic mode characterized by the propagation direction of $\overline{N}$ and the polarization direction $\overline{U}$ follows from Eqs. (A1) to (A4) up to terms linear in ϵ as

$$\Delta c(\overline{N}, \overline{U}) = \left\{ 2C_{jrqs} H_{qk} + C_{jrksmn} H_{mn} \right\} U_j U_k N_r N_s \epsilon \quad . \tag{A5}$$

When referred to a Cartesian coordinate system with axes parallel to the crystallographic axes of the cubic prototype phase, the tensor H_{ij} is for the cubic to tetragonal transition in Nb_3Sn (without volume change) given by

$$(H_{ij}) = \begin{Bmatrix} \frac{1}{2} & 0 & 0 \\ 0 & \frac{1}{2} & 0 \\ 0 & 0 & -1 \end{Bmatrix} \quad , \tag{A6}$$

provided the tetragonal axis lies in the x_3 direction. The corresponding values pertaining to the orientation of the tetragonal axis in the x_1 and x_2 directions are obtained by cyclic permutation of the diagonal elements in Eq. (A6). By substituting $\overline{N} = (1/\sqrt{2}, 1/\sqrt{2}, 0)$ and $\overline{U} = (0,0,1)$ into Eq. (A5) one obtains in conjunction with Eq. (A6) (and cyclic permutations) for the elastic constant increment of the associated shear modulus c_{44} the expressions

$$\Delta c_{44} = [c_{44} + \tfrac{1}{4}(c_{166} - c_{144})]\epsilon \quad , \tag{A7a}$$

$$\Delta c_{44} = -2[c_{44} + \tfrac{1}{4}(c_{166} - c_{144})]\epsilon \quad . \tag{A7b}$$

Here Eqs. (A7a) and (A7b) refer to the configuration with the tetragonal axis in the x_1 or x_2 direction, and in the x_3 direction, respectively. In Eqs. (A7a) and (A7b) the TOE constants have been expressed in Voigt notation according to the definition of Brugger.[33] Since for the shear modulus c_{44} there is no difference between adiabatic and isothermal values the TOE constants in Eqs. (A7a) and (A7b) are isothermal values.

If f_1, f_2, and f_3 (with $f_1 + f_2 + f_3 = 1$) denote the volume fractions of tetragonal domains in a multidomain crystal along the respective coordinate directions, and if additivity of the individual domain contributions is assumed one obtains for the shear-modulus increment of a multidomain crystal:

$$\Delta c_{44} = (1 - 3f_3)[c_{44} + \tfrac{1}{4}(c_{166} - - c_{144})]\epsilon \quad . \tag{A8}$$

Setting $f_3 = f$ and allowing for the sign change implied in the definition of Δc_{44} in Eq. (7) as shear-modulus decrement completes the derivation of Eq. (7).

Improvements of Eq. (A8) would have to include deviations from additivity of the individual domain contributions and would have to take into account details of the domain configuration.

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