We believe that this is presently the highest electrical conductivity exhibited by complexed metal atoms. A previous report of $10^{-3}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ for the electrical conductivity was based on a two-probe measurement using silver paste and mercury electrodes.[4] We have found Aquadag to be the most reliable contact for this material.

We have also measured the Seebeck coefficient against copper and found a room-temperature value of $+12\ \mu\mathrm{V}/{}^\circ\mathrm{K}$ (where the sign is for the cold junction). In the simplest interpretation, the low positive value would indicate a degenerate gas of holes.

It is interesting to note that these long-chain complexes are structurally similar in many respects to a model organic compound for a high-temperature one-dimensional superconductor proposed by Little.[12] Based on the closer metal-metal distances of the other complexes listed in Table I and the uncertain purity of the cyanide complexes, there is reason to believe that long chain complexes such as these should have even higher electrical conductivity than found here.

We are presently continuing our studies on the temperature dependence of the electrical conductivity, Seebeck effect, and Hall effect of $K_2Pt(CN)_4Br_{0.3}\cdot 2.3H_2O$ as well as of $Ir(CO)_{2.9}Cl_{1.1}$ and $Mg_{0.82}[Pt(C_2O_4)_2]\cdot 5.3H_2O$ and will report on the results in the near future.

The authors would like to acknowledge the many enlightening discussions with Aaron Bloch and his solid-state chemistry group.

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Evidence for a First-Order Structural Transformation in Nb_3Sn

L. J. Vieland and Roger W. Cohen
RCA Laboratories, Princeton, New Jersey 08540

and

Walther Rehwald
Laboratories RCA Ltd., Zurich, Switzerland

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We present experimental evidence that the structural transformation observed in Nb_3Sn is first order, as predicted by theories which invoke a band Jahn-Teller mechanism for the lattice instability. The magnitude of the spontaneous lattice distortion at the transition temperature is in excellent agreement with the theory.

The nature of the structural transformation in the β-W compounds V_3Si and Nb_3Sn has been the subject of considerable theoretical and experimental interest. Calculations based on independent electron sub-band models have unambiguously predicted that the cubic-to-tetragonal transition is first order, weakly so for V_3Si[1] but quite strongly for the case of Nb_3Sn.[2] However, the absence of an observable latent heat[3] and hysteresis[4] at the transition has been interpreted as evidence that the transformation is actually second order. Since a transition in which the tetragonal strain $\epsilon = \frac{2}{3}(1-c/a)$ is the only order parameter is necessarily first order,[5] the possibility of the existence of a second order parameter which is coupled to ϵ has been explored. Soft optic modes of particular symmetries have been proposed,[6] and calculations[7] based on a successful band model have predicted instabilities in these modes. Thus far, no direct experimental evidence for such an instability exists. Recently, Pytte[8] has reformulated the theory for acoustic modes, using a dynamic approach which can be employed to extend earlier calculations to wave numbers $q > 0$. In the $q = 0$ limit, this formulation is equivalent to earlier theories[1, 2] and yields, contrary to Pytte's assertion, a first-order transition. In this Letter we present experimental evidence which indicates that the transformation is indeed first order with a large spontaneous tetragonal strain at the transition, in excellent agreement with theory.[2]

The experimental quantities which are of interest here are the tetragonal strain $\epsilon(T)$ and the elastic constant for the soft shear mode $C_{11}(T) - C_{12}(T)$. On the basis of a constant-density-of-states model $C_{11}(T) - C_{12}(T)$ has been calculated for both the cubic[9] and tetragonal[10] lattice states. The strain $\epsilon(T)$ is obtained by differentiation of the free-energy expression given in Ref. 2 and formed the basis for the calculation of $\epsilon(T)$ for Nb_3Sn given there. The solutions for $\epsilon(T)$ give all the extrema in the free energy, which are shown schematically in Fig. 1. The range over which a solution is a relative maximum, relative minimum, or absolute minimum is obtained from an investigation of the free energy and is indicated in the figure. In connection with Fig. 1, we note the following important conclusions: (1) The state of lowest free energy involves a discontinuous jump in the value of $\epsilon(T)$ from zero to a finite positive[11] value at a transition temperature T_c. (2) The cubic state $\epsilon = 0$ is metastable below T_c down to a minimum supercooling temperature T_{SC}, where the cubic-state elastic $C_{11} - C_{12}$ vanishes, and the tetragonal state $\epsilon > 0$ is metastable above T_c up to a maximum superheating temperature T_{SH}. (3) Since $T_c > T_{SC}$, the elastic constant $C_{11} - C_{12} > 0$ at $T = T_c$ [12]

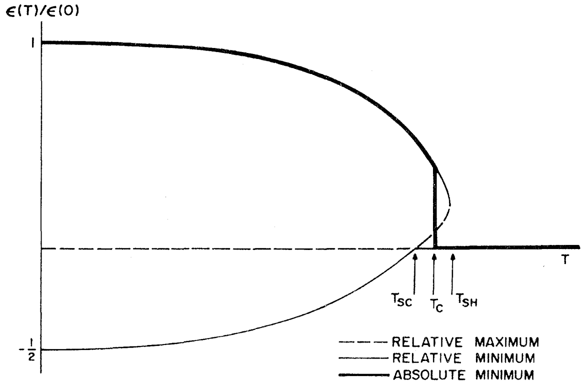

FIG. 1. Schematic behavior of the tetragonal strain $\epsilon = \frac{2}{3}(1 - c/a)$ as a function of temperature. The light, dashed, and heavy lines give values of the strain corresponding to various extrema in the free energy.

The essential questions left unanswered by previous x-ray[4] and elastic-constant[10] measurements on Nb_3Sn are these: (1) Does a region of forbidden values of the tetragonality exist in accordance with theoretical predictions, and (2) does the transformation occur when the elastic constant $C_{11} - C_{12}$ is nonzero, as discussed in the previous paragraph? We have performed x-ray diffraction and sound-velocity measurements on Nb_3Sn, which provide affirmative answers to both questions. The measurements were made on a large single crystal previously used for elastic-constant[10] and specific-heat[3] studies. The use of the same specimen for both experiments avoids difficulties due to the known sensitivity[3] of the transformation to material characteristics.

X-ray-diffraction profiles[13] from an extended $\{100\}$ face are shown in Fig. 2. On cooling from approximately 53°K the 14, 0, 0 peak begins to shift to higher angles with slight broadening. Observations of the internal $\{12, 8, 0\}$ reflections reveal that the peak shift is not due to a decrease in unit-cell volume, but is consistent with tetragonal symmetry with the developing c axis lying along the crystal face normal. The crosses of the figure give the tetragonal strain $\epsilon = a_0/c - 1$, where $a_0^3 = a^2c$ is the cell volume. For $T \leq 45.5$°K, wings appear on the central peak. The wings arise from tetragonal domains with tetrad axes lying along the three principal directions, except for small tilts of the order of 0.1°. The tetrago-

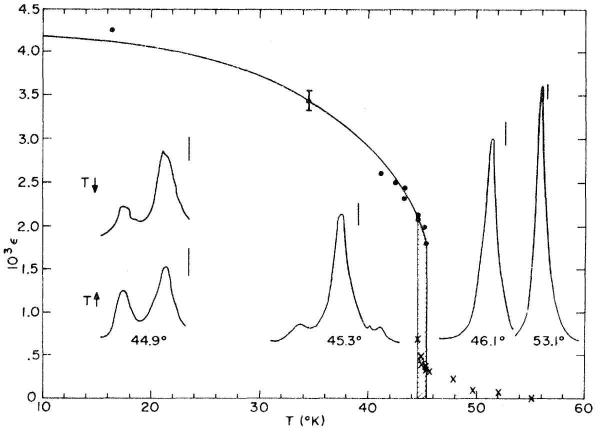

FIG. 2. X-ray diffraction profiles of the 14, 0, 0 Mo K_α peak and the strain ϵ vs T. The vertical lines near the peak maxima are fiducial marks. The crosses give the shift in the high-T peak and the circles indicate the tetragonality of the wing (domain) peaks. The solid line is a theoretical curve obtained from the free-energy function and parameters of Ref. 2 with $T_c = 45.5$°K.

nality of the domains is shown by the circles. The contribution of the wings to the total intensity grows rapidly with decreasing T, while that of the central peak diminishes. The region of coexistence of readily resolvable central and wing peaks is indicated roughly by the shaded area in the figure. The bulk of the transformation takes place in the temperature range $44.5°K < T < 45.5°K$. For $T < 44.5°K$, the central peak moves to higher angles and finally disappears at about 40°K. The absence of broadening of the diffraction peaks below 45.5°K indicates that no tetragonalities between those given by the peaks are present.

The highest temperature for which a domain structure is observed is $(45.5 \pm 0.2)°K$ independent of thermal history. For $T < 45.5°K$, the relative contribution of the domain structure is larger upon approaching the transformation from below. The pair of tracings at 44.9°K shows a typical dependence of the intensities of the central and high-angle peaks upon thermal history. The bottom trace was taken after cooling to 16°K and heating to 44.9°K. The crystal was then heated to 47°K and recooled to 44.9°K resulting in the upper pattern with a diminished central-peak intensity. There is no evidence of hysteresis in peak position, in agreement with previous observations.[4]

The theoretical curve of $\epsilon(T)$ vs T, calculated for a constant-density-of-states model with the parameters of Ref. 2 and $T_c = 45.5°K$, is also shown in Fig. 2. Excellent agreement between theory and experiment is found for all $T < 45.5°K$. Particularly gratifying is the agreement for the value of the spontaneous strain $\epsilon(T_c)$. The precursor strain above T_c is unexpected. Measurements on a similar, but polycrystalline, specimen showed a transformation to a domain structure at 52°K with a similar value of $\epsilon(T_c)$. A far smaller precursor strain above the transformation was observed, and the central peak was found to persist with diminished intensity down to the lowest temperature reached (10°K). A precursor was not observed in previous x-ray measurements[4] on single-crystal Nb_3Sn. Thus, the precursor appears to be strongly sample dependent.

Previous measurements[10] of the elastic constants for the crystal of Fig. 2 indicated that $C_{11} - C_{12}$ extrapolates to zero at $T = 49°K$. This temperature does not correspond to either the onset of the precursor or the transformation to the tetragonal domain state. We present evidence that $C_{11} - C_{12}$ is, in fact, nonzero at all temperatures. In Fig. 3 we show the behavior of the soft-mode elastic constant $C_{11} - C_{12}$ normalized to the temperature-independent lattice contribution[2] $A_{11} - A_{12}$. The crosses represent the data of Rehwald,[10] obtained directly from measurement of the velocity of the [110] shear mode with [1$\bar{1}$0] polarization. The wave could not be propagated below 52°K because of excessive attenuation. The solid circles were obtained by measuring the [100] longitudinal velocity, which gives C_{11}, and making use of the fact that the bulk modulus $(C_{11} + 2C_{12})/3$ is constant[10] below 100°K. This mode readily propagates down to 45.5°K where a large attenuation sets in, the signal vanishing a few tenths of a degree below 45°K. Above 62°K the two sets of data give identical results, as they should at all T for a crystal of cubic symmetry.

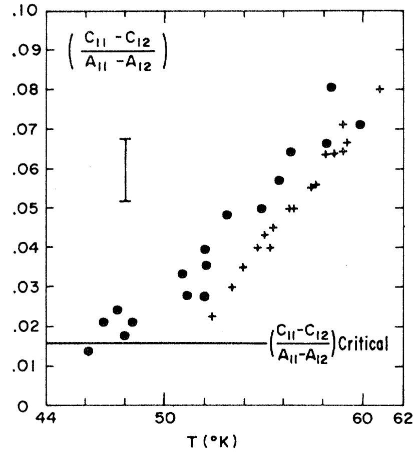

FIG. 3. Normalized soft-mode elastic constant $C_{11} - C_{12}$ vs T. The crosses are obtained from a direct measurement of the velocity of the [110] [1$\bar{1}$0] shear mode; the circles are deduced from the velocity of the [100] longitudinal mode C_{11}, with $C_{11} + 2C_{12} = \text{const}$. The error bar represents the scatter in the data for C_{11}, ±0.8%. The horizontal line gives the theoretical minimum value of the soft mode at the transformation.

The precursor strain and the discrepancy in the two methods of determining $C_{11} - C_{12}$ are attributed to sample inhomogeneity. Direct determination of the soft shear velocity from the relation $\langle v \rangle = l/t$, where l is the path length traversed by the sound pulse and t is the observed pulse transit time, gives an apparent elastic constant which tends to vanish in a manner determined by the softest part of the crystal in accordance with the relation $t = \int_0^l dr/v(r)$. On the other hand, the stiff C_{11} mode will be little affected by small variations in the elastic properties,[14] so that the deduced values of $C_{11} - C_{12}$ are more characteristic of the bulk of the crystal.

A quantitative connection between the elastic-constant and the x-ray data can be obtained from the theory. Equating the free energy[2] of the tetragonal and cubic phases gives the value of the elastic constant for which $T=T_c$, $(C_{11}-C_{12})_{\rm crit} \cong 0.016(A_{11}-A_{12})$. This critical value is shown by the horizontal line of Fig. 3; it represents the smallest value of the stiffness expected to be observed. The intersection of this line with the directly measured elastic constant (crosses) gives the maximum temperature at which tetragonality occurs, $T \cong 51$°K. This corresponds roughly to the temperature at which the first evidence of the lattice instability appears in the x-ray data as the precursor strain. We suppose, therefore, that the precursor strain represents the response of the crystal as a whole to small regions which are unstable with respect to tetragonal distortions. These regions are unable to achieve the full value of the spontaneous strain $\epsilon(T_c)$ because they are clamped by neighboring stable material. The precursor persists down to a temperature at which the bulk of the crystal has softened to the point where the spontaneous strain can be achieved. The crystal then breaks up into domains. This temperature is given by the intersection of the critical line with the deduced value of $C_{11}-C_{12}$, $T \cong 46$°K, in good agreement with the x-ray data. The range over which the transition is smeared is therefore reasonably accounted for by the band model. We note that the condition $C_{11}-C_{12}>0$ at T_c appears also to be fulfilled for the case[15] of V_3Si.

Our x-ray results enable us to understand the fact that the specific heat[3] for this sample shows a weak cusp at 44°K rather than the predicted latent heat. The nature of the transformation precludes the observation of a latent heat since the volume fraction of tetragonal domains goes continuously to zero as T_c is approached from below. This behavior is the same as that found[16] in $BaTiO_3$, which also shows a smeared first-order thermal transition. Above T_c the precursor strain gives rise to an additional specific heat, so that the overall anomaly is cusplike. The large temperature interval over which the transition is smeared and the fact that the specific heat is small compared to the lattice contribution make quantitative comparison with the theory difficult for this crystal.

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[11] The stable state $\epsilon(T)>0$, the sense of the observed transformation for Nb_3Sn, is the calculated one for the case in which the parameter G_{11} (Ref. 8) or U (Ref. 2) is positive. It is possible to adjust the sign of the transformation by including a term of third order in the strains in the free energy as in Ref. 1.

[12] Thus the transformation temperature specified by Pytte (Ref. 8) as $T_M = T_{SC}$ does not correspond to the state of lowest free energy.

[13] The experimental details will be published elsewhere.

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