Pressure-Enhanced Lattice Transformation in Nb_3Sn Single Crystal*

C. W. Chu
Department of Physics, Cleveland State University, Cleveland, Ohio 44115
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We report the first observation of pressure-enhanced lattice transformation in the high-temperature superconductor Nb_3Sn. The opposite pressure effects on the lattice transformation and the superconducting transition in A15 compounds can thus be understood on the basis of the Weger-Labbé-Friedel model by taking into account the pressure-induced interband charge transfer.

Many high-temperature superconductors exhibit a lattice transformation from cubic to tetragonal symmetry at temperature T_L above their superconducting transition temperature T_C. This concurrence of lattice transformation and high-temperature superconductivity has stimulated extensive investigations, both experimental and theoretical, on the two phenomena.[1] Hydrostatic pressure studies were recently made on T_L and T_C of near equiatomic V-Ru,[2] $(Hf_{1-x}Zr_x)V_2$,[3] and V_3Si[4] compounds. Without exception, T_L always decreases while T_C increases with pressure. In view of the negative pressure dependence of T_C in polycrystalline Nb_3Sn,[5] the determination of the pressure behavior of its T_L is particularly important in the understanding of lattice transformation and high-temperature superconductivity. We have determined calorimetrically the pressure dependence of T_L of an Nb_3Sn single crystal up to 18 kbar. For the first time, lattice transformation was observed to be enhanced by the application of hydrostatic pressure in a high-T_C superconductor. T_C was also measured inductively at different pressures. It is suppressed by pressure at the same rate as that previously observed for polycrystalline samples.[5]

An ac temperature-modulation technique[6] was employed to determine the temperature variation of the relative specific heat C_p and the temperature derivative R' of the resistance of the Nb_3Sn single crystal under hydrostatic pressure. It is a combination of the high-pressure clamp technique and an ac calorimetric method. The pressure medium was a fluid mixture of 1:1 n-pentane and isoamyl alcohol. A superconducting lead manometer situated next to the sample was used to measure the pressure at low temperature. The pressure change[7] due to cooling usually is small and was shown to occur mainly at the freezing of the pressure medium. The pressure medium used freezes at ~180 K at atmospheric pressure. Hence the quoted pressure is that determined at low temperature (7 K). The temperature of the sample was determined by a Au plus 0.07% Fe–Chromel thermocouple and/or a Ge thermometer depending on the temperature range.

The Nb_3Sn sample studied was part of the RCA single crystal which was observed[8] to transform at low temperature in the x-ray–diffraction and neutron-scattering experiments. The resistance ratio between 300 and 20 K was 7. The lattice transformation was clearly evidenced by anomalies in C_p, R', and resistance R. At atmospheric pressure, both in the absence and then in the presence of the pressure medium, T_L was found to be ~43 K which is ~2 degrees lower than that previously observed.[8] This may be due to the inhomogeneous nature[9] of the big crystal from which our small sample was cut. In Fig. 1, the temperature dependence of the relative C_p is shown at several pressures. The numbers underlined represent the sequential order of the experimental runs and the others stand for the pressure in kilobars. The arrow bars define the width of the lattice transformation, which varies from a few tenths of a degree at low pressure to about one degree at 18.3 kbar. Over the same temperature region, R exhibits a drop which gives rise to a large peak in R' corresponding to a change of over 100% at atmospheric pressure, as depicted in the inset of Fig. 1. However, at high pressure, e.g., >10 kbar, the R drop becomes sluggish and the R' peak degenerates into a broad jump. T_L defined above was plotted as a function of pressure in Fig. 2. It is enhanced by the application of hydrostatic pressure, linearly with $dT_L/dP = +(2.8 \pm 0.1) \times 10^{-4}$ kbar^{-1} for $P > 5$ kbar but nonlinearly at a higher rate for $P < 5$ kbar, in contrast to $dT_L/dP = -(1.5 \pm 0.1) \times 10^{-4}$ kbar^{-1} for V_3Si for pressures up to 18 kbar.[4] dT_L/dP is estimated to be $+(3.3 \pm 0.3) \times 10^{-4}$ kbar^{-1} as P approaches zero. In the same figure, the pressure dependence of T_c determined

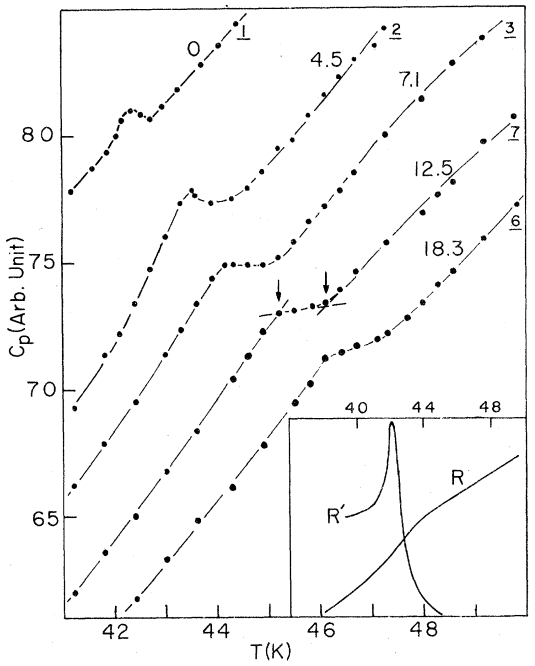

FIG. 1. Temperature dependence of the relative C_p at different pressures for Nb_3Sn single crystal. The inset shows the anomalies of resistance R and resistance slope R' at the T_L and atmospheric pressure.

inductively was shown to be $-(1.40\pm0.05)\times10^{-5}$ kbar^{-1}. This is identical to that recently measured calorimetrically.[10] Hence the T_C data so obtained are characteristic of the tetragonal phase of the sample. $|dT_C/dP|$ is 2–3 times smaller than that for V_3Si.[4]

It has been shown that many of the unusual physical properties at atmospheric pressure of high-T_C A15 compounds, such as Nb_3Sn and V_3Si, could be understood in the framework of the Weger-Labbé-Friedel (WLF) model.[11] According to this model, the band structure exhibits sharp and narrow density-of-states peaks at the d sub-band edges, characteristic of the linear-chain arrangement of the transition-metal atoms in the A15 compounds. The relative position of the Fermi level with respect to the band edge depends on the number of d electrons in the sub-band Q. The Q dependence of both T_L and T_C for cubic Nb_3Sn and V_3Si were calculated by Labbé, Barišić, and Friedel.[12] They found that T_L and T_C, instead of being monotonically varying functions of Q, peak at Q_{LM} and Q_{CM}, respectively, as shown in Fig. 3. T_L drops back to zero when $Q > Q_0$. Because of the larger Q and less localized atomic d orbital for Nb_3Sn, its Q_{LM}/Q_{CM} ratio was found to be >1 in contrast to the case of <1 for V_3Si. In addition, Labbé, Barišić, and Friedel[12] also estimated that $Q_{CM}\simeq Q< Q_{LM}$ for Nb_3Sn while $Q_{CM}> Q\simeq Q_{LM}$ for V_3Si. The application of hydrostatic pressure will undoubtedly bring the linear chains closer together and will thus lead to a redistribution of charges in different bands. Therefore the observed opposite pressure effects on T_L and T_C of Nb_3Sn and V_3Si can easily be understood qualitatively in terms of the WLF model, provided that pressure enhances Q of these compounds and that Q remains in between Q_{LM} and Q_{CM}. Any crossover between Q and Q_{LM} or Q_{CM} will result in a sign change of dT_L/dP or dT_C/dP. In addition, the observed smaller value of $|dT_L/dP|$ for V_3Si can be attributed to the close proximity of Q to Q_{LM}, and that of $|dT_C/dP|$ for Nb_3Sn to the close proximity of Q to Q_{CM}. It should be noted that the experimental T_C results of the transforming samples are for tetra-

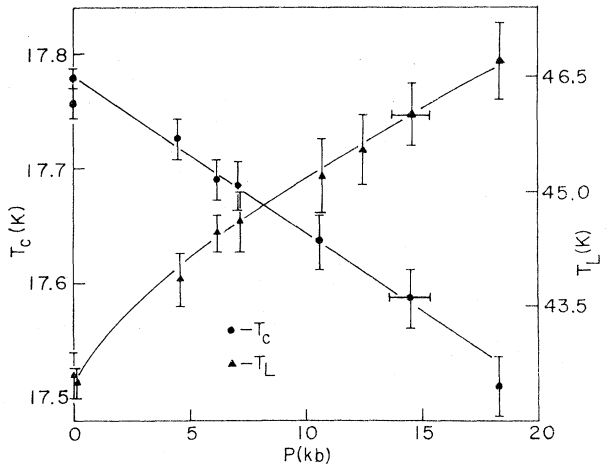

FIG. 2. Pressure dependence of T_L and T_C of Nb_3Sn single crystal.

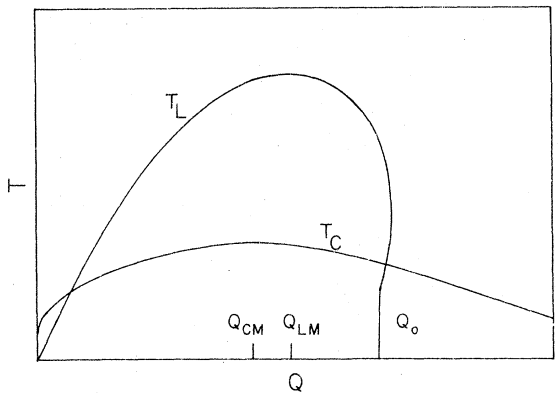

FIG. 3. Schematic variations of T_L and T_C with Q for Nb_3Sn (after Ref. 12).

gonal lattice[10] while the calculated T_C-Q relation is for the cubic lattice. However in view of the small effects[1,10,11] of the lattice transformation on the electronic properties of Nb_3Sn and V_3Si, we believe that the general T_C-Q behavior for the tetragonal lattice is similar.

Recently the temperature dependence of the pressure coefficient of the shear modulus of V_3Si was observed[13] to decrease from a positive value to a negative minimum before reversing the sign back to positive at lower temperature. To explain this anomalous behavior and the negative dT_L/dP of V_3Si, it was proposed[4,14] that the WLF model should be extended to include effects due to the pressure-induced interband charge transfer. By fitting the experimental data, Ting and Ganguly and Barsch and Rogowski found[4] that pressure indeed enhances Q. Using Ting and Ganguly's estimate, we found that at 20 kbar Q increases by ~10% but still lies below Q_{CM}, in agreement with the observation of positive dT_C/dP at this pressure.[15] According to this model, a pressure of ≥ 34 kbar is needed to raise Q to above Q_{CM} such that dT_C/dP changes to negative sign. Earlier it[4] was determined through extrapolation that ~24 kbar is sufficient to stabilize the cubic lattice in V_3Si, suggesting that $Q_0 < Q_{CM}$, consistent with the recent observation of positive dT_C/dP for both the transforming and nontransforming V_3Si samples.[16] On the other hand, Labbé, Barišić, and Friedel[12] obtained $Q_0 > Q_{CM}$. This disagreement may be attributed to the uncertainties associated with the physical parameters used in their calculation. Lack of experimental data prevents us from making a similar comparison for Nb_3Sn. However a discussion of the experimental results at atmospheric pressure of doped Nb_3Sn in terms of the WLF model is worthwhile. For $Nb_3Sn_{1-x}Al_x$,[17] a slight replacement of Sn by Al results in a decrease of Q and hence a decrease of T_L but an increase of T_C, as was observed. With large x, e.g., ≥ 0.08, the lattice remains cubic below T_C, while T_C still increases. This absence of lattice transformation may arise from the higher density of imperfections in the crystal lattice, as for the case of V_3Si.[18] However for $Nb_3Sn_{1-x}Sb_x$,[19] the substitution of Sb for Sn not only increases Q but also changes the ratio c/a from <1 to >1. The ratio Q_{LM}/Q_{CM} may consequently shift from >1 to <1. The observed x-independent T_L and x-decreasing T_C are thus not unlikely. Studies of T_L and T_C of these samples under hydrostatic pressure, where presumably only Q variation is important, are planned to check the explanation of the doped-Nb_3Sn results, suggested above.

Recently Ting and Ganguly[14] calculated the isothermal pressure coefficient $(\partial C_s/\partial P)_T$ of the shear modulus C_s, on the basis of the WLF model. By extending their formalism and using their notation, we have obtained an expression for dT_L/dP. T_L is defined as the temperature[12] at which the shear modulus C_s vanishes, i.e.,

$$C_s(T_L) = 0 = \tfrac{1}{2}Na^2q^2\int_{-|E_0|}^{|E_0|} dE\, nE(f + E\partial f/\partial E) + C_s', \tag{1}$$

subject to the constraint

$$Q = \int_{-|E_0|}^{|E_0|} dE\, nf, \tag{2}$$

where $n = (4/\pi)[2|E_0|(|E_0|+E)]^{-1/2}$ is the density of states of the d sub-band; $f = [1+\exp(E-E_F)/kT_L]^{-1}$, the Fermi function at T_L with Fermi energy E_F; $3N$ is the number of transition metal atoms per unit volume; a is the interatomic distance, q the Slater coefficient of the atomic d orbital, $|E_0|$ the half-width of the d sub-band, and C_s' the temperature-independent part of C_s. Under pressure, with strain $\epsilon = \kappa P/3$, $N \to N(1+3\epsilon)$, $|E_0| \to |E_0|\exp(aq\epsilon)$, $a \to a(1-\epsilon)$, $T_L \to T_L + (\partial T_L/\partial\epsilon)\epsilon$, and $Q \to Q + \delta Q$. By keeping only the first-order terms of ϵ in the Taylor's expansion of Eq. (1), we have

$$\frac{\partial \ln T_L}{\partial P} = +\frac{\tfrac{1}{6}N\kappa a^2q^2\int_{-|E_0|}^{|E_0|} dE\, nE[(1+aq)f + (1+2aq)E\partial f/\partial E + (aqE - \partial E_F/\partial\epsilon)(\partial f/\partial E + E\partial^2 f/\partial E^2)] + \partial C_s'/\partial P}{\tfrac{1}{2}Na^2q^2\int_{-|E_0|}^{|E_0|} dE\, nE[(E-E_F)(\partial f/\partial E + E\partial^2 f/\partial E^2) + E\partial f/\partial E]}. \tag{3}$$

The term $\partial E_F/\partial\epsilon$ in Eq. (3) is determined by Eq. (2), allowing $Q \to Q + \delta Q$ under stress. It is interesting to note that the numerator can be identified with $(\partial C_s/\partial P)_{T_L}$[14] and the denominator with $-T_L(\partial C_s/\partial T)_P$ provided $\partial E_F/\partial T$ is negligibly small. Hence Eq. (3) is reduced to the familiar form $(\partial T_L/\partial P) = -(\partial C_s/\partial P)_{T_L}(\partial C_s/\partial T)_P^{-1}$ whose validity has been demonstrated for V_3Si.[14] Lack of information about $\partial C_s/\partial P$ for Nb_3Sn makes the determination of δQ and consequently of $\partial E_F/\partial\epsilon$ very difficult. No attempt is made at using Eq.

(3) for any numerical calculation of $\partial T_L/\partial P$ for Nb_3Sn. A similar calculation on dT_C/dP, including the interband charge-transfer effect, can be done.

In conclusion, we have observed for the first time pressure-enhanced lattice transformation in a high-T_C superconductor. The opposite pressure effects on T_L and T_C of Nb_3Sn and V_3Si can be explained in terms of the WLF model by taking into account the pressure-induced interband charge transfer. Previous atmospheric results on T_L and T_C of doped Nb_3Sn samples were discussed and an expression for dT_L/dP was also obtained.

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[1]For a review see L. R. Testardi, in *Physical Acoustics*, edited by W. P. Mason and R. N. Thurston (Academic, New York, 1974), Vol. X.

[2]C. W. Chu and T. F. Smith, Bull. Amer. Phys. Soc. 17, 311 (1972); T. F. Smith, R. N. Shelton, A. C. Lawson, and C. W. Chu, to be published.

[3]T. F. Smith, R. N. Shelton, and A. C. Lawson, J. Phys. F: Metal Phys. 3, 2157 (1973).

[4]C. W. Chu and L. R. Testardi, Phys. Rev. Lett. 32, 766 (1974).

[5]H. Neubauer, Z. Phys. 266, 211 (1969); T. F. Smith, J. Low Temp. Phys. 6, 171 (1972).

[6]C. W. Chu and G. S. Knapp, Phys. Lett. 46A, 33 (1973).

[7]A. Sawaoka and N. Kawai, Jpn. J. Appl. Phys. 9, 353 (1970).

[8]R. Mailfert, B. W. Batterman, and J. J. Hanak, Phys. Status Solidi 32, K67 (1969); G. Shirane and J. D. Axe, Phys. Rev. B 4, 2957 (1971).

[9]L. J. Vieland and A. W. Wicklund, Solid State Commun. 7, 37 (1969).

[10]C. W. Chu and L. J. Vieland, to be published.

[11]For a review see M. Weger and I. B. Goldberg, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1974), Vol. 28.

[12]J. Labbé, S. Barišić, and J. Friedel, Phys. Rev. Lett. 19, 1039 (1967); J. Labbé, Phys. Rev. 172, 451 (1968).

[13]P. F. Carcia, G. R. Barsch, and L. R. Testardi, Phys. Rev. Lett. 27, 944 (1971); P. F. Carcia and G. R. Barsch, to be published.

[14]C. S. Ting and A. K. Ganguly, Phys. Rev. B 9, 2781 (1974); G. R. Barsch and D. A. Rogowski, to be published.

[15]T. F. Smith, Phys. Rev. Lett. 25, 1483 (1970); H. Neubauer, Z. Phys. 226, 211 (1969).

[16]S. Huang and C. W. Chu, Bull. Amer. Phys. Soc. 19, 228 (1974), and to be published.

[17]L. J. Vieland and A. W. Wicklund, Phys. Lett. 34A, 43 (1971).

[18]S. J. Williamson, H. Fung, and C. S. Ting, Phys. Rev. Lett. 32, 9 (1974).

[19]L. J. Vieland, J. Phys. Chem. Solids 31, 1449 (1970).

Variation of T_c with Electron-per-Atom Ratio in Superconducting Transition Metals and Their Alloys

I. R. Gomersall and B. L. Gyorffy
H. H. Wills Physics Laboratory, Royal Fort, Bristol BS8 1TL, United Kingdom
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A microscopic explanation is given for the variation of the superconducting transition temperature T_c with the electron-per-atom ratio in transition metals and their alloys.

As was first noted by Matthias,[1] if one plots the superconducting transition temperature T_c against the electron-per-atom ratio ϑ for various metals, one obtains a two-peaked curve with maxima at $\vartheta \simeq 4.5$ and at $\vartheta \simeq 6.5$ and a deep minimum at $\vartheta \simeq 5.5$. This is the most consistently obeyed empirical rule relating T_c to a normal-state property and it has often proved to be of practical significance in searches for high-T_c materials.[2] The purpose of this note is to provide a first-principles understanding of how such behavior arises as a consequence of interactions between electrons and phonons in a metal.

According to McMillan's solution of the strong-coupling gap equation[3]

$$T_c = \frac{\langle\omega\rangle}{1.2} \exp\left\{-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right\}, \quad (1)$$

where μ^* is an electron-electron interaction parameter which may be set equal to 0.13 for all