Solids 2, 40 (1970).
[22]Trademark of the Fluorocarbon Co., Pine Brook, N. J. 07058.
[23]F. Horner, T. A. Taylor, R. Dunsmuir, J. Lamb, and W. Jackson, Proc. IEEE 93, 11153 (1946).
[24]F. Eckart and H. Rabenhorst, Ann. Physik 19, 381 (1956).
[25]B. T. Kolomiets, Phys. Status Solidi 7, 713 (1964).
[26]A. Leiga (unpublished).
[27]J. S. Berkes and J. Hillegas (private communication).
[28]T. J. Dowd, Proc. Phys. Soc. (London) 64, 783 (1951).
[29]E. J. Felty, G. Lucovsky, and M. B. Myers, Solid State Commun. 5, 555 (1967).
[30]R. F. Shaw (private communication).
[31]P. C. Taylor, G. A. Bishop, and D. L. Miller, in International Conference on the Physics of Semiconductors, Boston, 1970 (unpublished).
[32]L. K. H. VanBeek, Progr. Dielectrics 7, 69 (1967).
[33]J. A. Simmons, G. S. Nadkarin, and M. C. Lancaster, J. Appl. Phys. 41, 588 (1970).
[34]B. Binggeli and M. Kiess, J. Appl. Phys. 38, N984 (1967).
[35]M. Pollak, Phys. Rev. 138, A1822 (1965).
[36]J. L. Hartke and P. J. Regensburger, Phys. Rev. 139, A970 (1965).
[37]A. I. Lakatos and J. Mort, Bull. Am. Phys. Soc. 14, 737 (1969); J. Mort and A. I. Lakatos, J. Non-Cryst. Solids 4, 391 (1970).
[38]M. H. Cohen, J. Non-Cryst. Solids 4, 391 (1970).
[39]W. L. Lacourse, V. A. Twaddell, and J. D. Mackenzie, J. Non-Cryst. Solids 3, 234 (1970).
[40]M. D. Tabak, Phys. Rev. B 2, 2104 (1970).

PHYSICAL REVIEW B VOLUME 3, NUMBER 6 15 MARCH 1971

Analysis of the Grüneisen Parameter for Cu and Associated Force-Model Calculations for Cu and Ag

Joseph L. Feldman and Earl F. Skelton
U. S. Naval Research Laboratory, Washington, D. C. 20390
(Received 26 October 1970)

An analysis of the temperature dependence of the thermodynamic Grüneisen parameter γ_I of Cu is performed in order to obtain the values of $\gamma_D(n)$, essentially the volume derivatives of the nth moments of the phonon spectrum. Simple phenomenological force-model calculations of $\gamma_I(T)$ and $\gamma_D(n)$, which principally make use of the pressure derivatives of the elastic constants and published "harmonic" force models obtained from neutron-diffraction data, have also been performed for Cu and Ag. The sensitivity of the results of the force-model calculations to the various quoted values of the second-order force constants and the pressure derivatives of the elastic constants is indicated. Comparison is made with experiment wherever possible.

INTRODUCTION

As discussed by Barron *et al.*,[1] an appropriate analysis, based on the quasiharmonic approximation, of the thermodynamic Grüneisen parameter $\gamma_I(T)$, yields information about the volume dependences of several moments of the vibrational frequency distribution. It seemed worthwhile to perform this analysis for Cu,[2] although the temperature dependence of γ_I for Cu is somewhat weaker than it is for substances used in previous analyses.[3] We point out that these types of analyses may be useful for accurately determining volume dependences of the Debye-Waller factor or specific heat, since in the quasiharmonic approximation these quantities are describable in terms of moments of the frequency spectrum over wide temperature regions. Partly for the purpose of comparison with our analysis for Cu, we have also performed related calculations based on simple phenomenological force models appropriate to Cu and Ag.

A theoretical evaluation of $\gamma_I(T)$, in the quasiharmonic approximation, chiefly requires a knowledge of second-order force constants and their volume dependences. Very recently Sharma and Singh[4] have presented results of calculations of $\gamma_I(T)$ for the noble metals based on the Chéveau model,[5] which explicitly takes into account the electron-gas contribution to the force constants in an approximate way. The potential parameters involved in their calculations were determined according to the method of long waves, using the measured values of the adiabatic elastic constants at each temperature of interest and the pressure derivatives of these constants at room temperature. We have performed similar force-model calculations of both $\gamma_I(T)$ and $\gamma_D(n)$, essentially the volume derivative of the nth moment of the frequency distribution. Our model involves published second-order force constants determined from neutron data[6-8] and the assumption that the volume derivatives of further than nearest-neighbor force constants can be neglected. The

values of the remaining volume derivatives are determined, by the method of long waves, principally[9] from the measured values of the pressure derivatives of the room-temperature adiabatic elastic constants dc_{ij}/dP.[10–13] It was of some interest to perform calculations on the basis of this model for Cu and Ag because it has been found empirically that the force constants between nearest-neighbor atoms are dominant[6–8] and because "reasonable" values of the parameters of the short-range Born-Mayer potential are obtainable from measurements of the third-order elastic constants for these metals.[14] The parameters of our models are determined mainly from room-temperature data except when noted, because these appear to be the most accurate and complete data. Of course, it would be preferable to make use of low-temperature data, but it is expected that the use of such data[15] would not affect our results greatly. Finally, it should be mentioned that many other workers have performed calculations relating to $\gamma_l(T)$ for the noble metals,[13,14,16,17] but the models used differ substantially from ours and no force-model calculations of $\gamma_D(n)$ for noble metals have appeared in the literature to our knowledge.

THEORY

We are primarily concerned with the quantities $\gamma_l(T)$ and $\gamma_D(n)$ as given by their usual expressions[18]

$$\gamma_l(T) \equiv \frac{V}{C_{v,l}} \frac{\partial S_l}{\partial V} \approx \sum_j \gamma_j c(\omega_j, T) / \sum_j c(\omega_j, T) \quad (1)$$

and

$$\gamma_D(n) \equiv \frac{\sum_j \gamma_j \omega_j^n}{\sum_j \omega_j^n} = -\frac{1}{n} \frac{\partial \ln \overline{\omega^n}}{\partial \ln V}, \quad n \begin{cases} > -3 \\ \neq 0 \end{cases} \quad (2)$$

where ω_j is the frequency associated with the jth normal mode, γ_j is the mode Grüneisen parameter, $c(\omega_j, T)$ is the contribution of the jth normal mode to the heat capacity, and ω^n is the nth moment of the frequency distribution.[19] Further, the quasiharmonic approximation is made in obtaining the equality in expression (1) and S_l and $C_{v,l}$ denote the lattice-vibrational contributions to the entropy and isochoric heat capacity, respectively. It might also be mentioned here that, for metals, in order to obtain $\gamma_l(T)$ from the quantity which is determined directly from experimental data, i.e., $\gamma(T) = \beta V / K_T C_v$, where β is the volume expansivity, V is the volume, K_T is the isothermal compressibility, and C_v is the isochoric heat capacity, it is necessary to take account of the effects in β and C_v of the electronic excitations. The quantity $\gamma_l(T)$ may then be analyzed with the aid of the latter equality in expression (1) for the purpose of obtaining values of $\gamma_D(n)$.[20]

With regard to our force-model calculations, the indicated sums in expressions (1) and (2) were performed with the aid of a uniform cubic grid of 2992 points in $\frac{1}{48}$ of the Brillouin zone. The accuracy of the results increases rapidly with increasing T [for $\gamma_l(T)$] and increasing n [for $\gamma_D(n)$] and is better than 1% for $n = -2.5$ and $T = 5\,^\circ\mathrm{K}$; this is an estimate based on the comparison of results for grids of 2992 and 408 points in $\frac{1}{48}$ of the Brillouin zone. The mode Grüneisen parameter was obtained at arbitrary points in the Brillouin zone with the use of the expression[21]

$$\gamma_j = -\frac{\partial \ln \omega_j}{\partial \ln V} = \frac{-V}{2\omega_j^2} \sum_{\alpha,\beta} \hat{e}_\alpha(j) \frac{\partial D_{\alpha,\beta}(\vec{f})}{\partial V} \hat{e}_\beta(j), \quad (3)$$

where $\hat{e}_\alpha(j)$ and $D_{\alpha,\beta}(\vec{f})$ correspond to the polarization vector and dynamical matrix, respectively, and where $\vec{f}$ denotes the wave vector and i denotes the polarization index of the mode. We also note here that volume derivatives of only the interatomic force constants enter Eq. (3), as can be easily seen from the form of the dynamical matrix for Bravais crystals.[21]

THERMODYNAMIC DATA

The thermal-expansion data used in evaluating $\gamma_l(T)$ for Cu were taken from several sources. In the low-temperature region ($6 < T \leq 30\,^\circ\mathrm{K}$) the data of Carr, McCammon, and White[22] were used; the error in their results is estimated to be within ±5% at 7 °K and within 1% above 15 °K. Their determination of the electronic coefficient of linear expansion was also employed: $\alpha_e = 1.45 \times 10^{-10} T\ ^\circ\mathrm{K}^{-1}$ (±10%), where T is in °K. It is to be noted that the results of Carr *et al.*[4] are essentially in agreement with the recent low-temperature measurements of Kos and Lamarche.[23] There have been several recent publications of the thermal expansivity of Cu in the range $30 < T < 300\,^\circ\mathrm{K}$: Rubin *et al.*,[24] Bijl and Pullan,[25] Simmons and Balluffi[26] ($T < 100\,^\circ\mathrm{K}$), and Leksina and Novikova[27] ($90\,^\circ\mathrm{K} < T$). All these data agree with each other to within less than 2%, except for the data of Bijl and Pullan,[25] whose result at 40 °K is more than 30% below the corresponding results reported in the other three papers. Simmons and Balluffi[26] have suggested that the capacitor dilatometer technique employed by Bijl and Pullan has a systematic error at low temperatures. Thus we have discounted the data of Bijl and Pullan. We have used only the data of Rubin *et al.*[24] in the range ($30 < T \leq 90\,^\circ\mathrm{K}$) and the data of Leksina and Novikova[27] in the range ($90 < T \leq 300\,^\circ\mathrm{K}$) for determining the values of $\gamma_D(n)$, since these data are in good agreement in their region of overlap; i.e., the agreement is within 1%

at $T = 90\,^{\circ}\mathrm{K}$ and within 0.5% at $T = 280\,^{\circ}\mathrm{K}$, and since the data of Rubin *et al.*[24] are in good agreement with the low-temperature measurements of Carr *et al.*[22] However, our error estimates are based on the spread of the thermal-expansion data corresponding to the different measurements which we have considered; use of the individual estimates of accuracy quoted by Rubin *et al.*[24] and Leksina and Novikova[27] would lead to much smaller error bars in $\gamma_D(n)$.

Values of the remaining quantities (and their limits of accuracy) which enter into $\gamma(T)$ for Cu were obtained from the ultrasonic measurements of Overton and Gaffney[28] and the specific-heat compilation of Furukawa *et al.*[29] We mention, too that values of the moments of the frequency distribution which are needed in our analysis were obtained from the analysis of the heat capacity of Cu by Barron *et al.*[30]

RESULTS AND DISCUSSION

The results of our calculations are shown in Figs. 1–4. Since there exist several sets of experimental values of the pressure derivatives of the elastic constants,[10–13] we present force-model calculations for each set of values. Furthermore, several harmonic force models[6–8] which serve as reasonably accurate representations of the dispersion curves for Cu have appeared in the literature, so we have performed our calculations for a few of these harmonic models. Hopefully, our calculations provide an indication of the uncertainties in calculated $\gamma_I(T)$ curves for Cu and Ag arising from uncertainties in values of dc_{ij}/dP and, in the case of Cu, in neutron

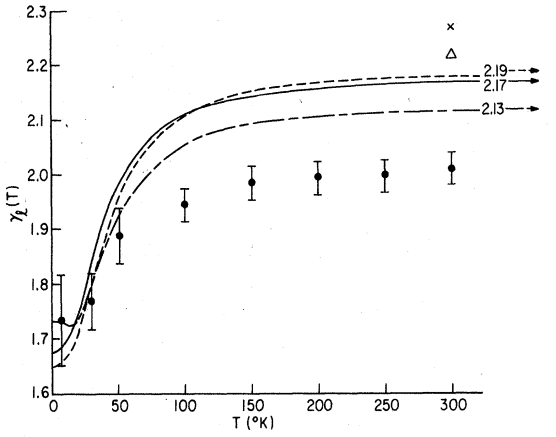

FIG. 1. $\gamma_I(T)$ for Cu. The solid, broken, and dashed curves correspond to a sixth-neighbor harmonic model based on $T \approx 300\,^{\circ}\mathrm{K}$ neutron data and to model parameters obtained with the use of experimental values of the pressure derivatives of the $T \approx 300\,^{\circ}\mathrm{K}$ adiabatic elastic constants given by Hiki and Granato (Ref. 11), Daniels and Smith (Ref. 10), and Salama and Alers (Ref. 12), respectively; the high-temperature limiting values are also indicated. The triangle and cross correspond to the data of Salama and Alers (Ref. 12) used with a sixth-neighbor harmonic model (Ref. 7) based on $T = 49\,^{\circ}\mathrm{K}$ neutron data and a fourth-neighbor harmonic model (Ref. 6) based on $T = 300\,^{\circ}\mathrm{K}$ neutron data, respectively. The vertical bars represent the experimental values (see text).

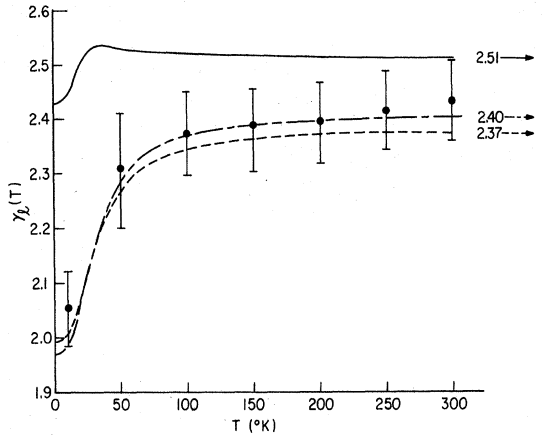

FIG. 2. $\gamma_I(T)$ for Ag. The solid, broken, and dashed curves correspond to a fourth-neighbor harmonic model based on $T \approx 300\,^{\circ}\mathrm{K}$ neutron data and to model parameters obtained with the use of pressure derivatives of the $T \approx 300\,^{\circ}\mathrm{K}$ adiabatic elastic constants given by Hiki and Granato (Ref. 11), Daniels and Smith (Ref. 10), and Ho *et al.* (Ref. 13), respectively; the high-temperature limiting values are also indicated. The vertical bars represent the experimental values obtained from thermal-expansion [Refs. 5 (the anomalous data reported for $T < 7\,^{\circ}\mathrm{K}$ were disregarded), 31, 32], compressibility (Ref. 33), and heat-capacity data (Ref. 29).

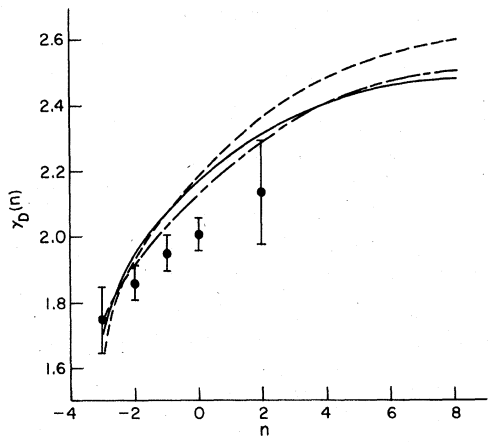

FIG. 3. $\gamma_D(n)$ for Cu. The description of the calculated curves in terms of the model parameters is the same as in Fig. 1. The calculations were performed at intervals in n of 0.5 for $n < 0$ and 1.0 for $n > 0$. The vertical bars represent the estimated errors of our determination of $\gamma_D(n)$ essentially from the experimental values of $\gamma(T)$.

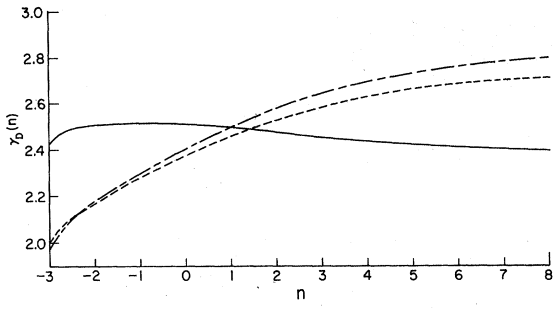

FIG. 4. $\gamma_D(n)$ for Ag. The description of the calculated curves is the same as in Fig. 2. The calculations were performed at intervals in n of 0.5 for $n<0$ and 1.0 for $n>0$.

measurements of the dispersion curves. As seen in Fig. 1, only the calculations based on the Daniels-Smith[13] values of dc_{ij}/dP and the sixth-neighbor ($T=300\,^\circ$K) model[7] yield an initial decrease of $\gamma_j(T)$ with increasing temperature. All other results which we have obtained for $\gamma_l(T)$ for Cu appear to be in qualitative agreement with each other. For clarity, only values of $\gamma_l(T=300\,^\circ\text{K})$ calculated with the use of the fourth-neighbor ($T=300\,^\circ$K) model[6] and the sixth-neighbor ($T=49\,^\circ$K) model[7] are shown in the figure. It might also be mentioned that our results appear to be in reasonable agreement with the calculations of Sharma and Singh.[4]

Our results for $\gamma_l(T)$ for Ag indicate that the Daniels-Smith[10] values of dc_{ij}/dP lead to much closer agreement with experiment at moderate temperatures than do the Hiki-Granato[11] values, as concluded also by Sharma and Singh.[4] In addition, we have found that recent values of dc_{ij}/dP obtained by Ho *et al.*[13] yield excellent agreement with the experimental $\gamma_l(T)$ curve at moderate temperatures, as shown in Fig. 2. However, it should be stressed that, owing to the crudeness of our model and our neglect of certain anharmonic effects, our results do not imply that the measurements of Hiki and Granato[11] are in error.

We have also considered the effects on our model calculations of small uncertainties in the room-temperature elastic constants which, as can easily be shown, are needed in order to determine the volume derivatives of the force constants in the framework of our model. Our quoted results for Cu and Ag are based somewhat arbitrarily on the room-temperature elastic constants of Overton and Gaffney[28] and Hiki and Granato,[11] respectively. The use of the room-temperature elastic constants of Hibi and Granato[11] for Cu and of Neighbours and Alers[33] for Ag would cause constant changes in calculated Grüneisen parameters of only -1% and $+3\%$, respectively.

Values of $\gamma_D(n)$ for Cu and Ag are shown in Figs. 3 and 4, respectively. As seen in Fig. 3, the model calculations, which are in fair agreement with the results of the data analysis, yield a monotonically increasing $\gamma_D(n)$ curve for all values of n considered. We note that this behavior of $\gamma_D(n)$ differs qualitatively from what is found in the alkali halides where maxima in $\gamma_D(n)$ are predicted for $n\sim 2$.[1] We believe that the consistency of our results for $\gamma_D(n)$ tends to indicate that the methods and approximations used in our work are not grossly in error.

Finally, we wish to compare our force-model results for $\gamma_D(0)$, or γ_l^∞ [the value of $\gamma_l(T)$ in the high-temperature limit], with those of Hiki *et al.*,[14] which are based on the anisotropic continuum model and on $T=300\,^\circ$K input data. For Cu and Ag, Hiki *et al.*[14] obtained values of γ_l^∞ of 2.07 and 2.55, respectively, as compared to our values (based on the same data as those used by Hiki *et al.*, as far as possible) of 2.16 ± 0.02 and 2.51, where the ±0.02 takes into account the two $T=300\,^\circ$K harmonic models for Cu. Thus it is perhaps of some interest that both the continuum model and the models we use yield comparable results for γ_l^∞ of Cu and Ag, although the continuum model should not be expected to yield the correct temperature dependence of γ_l at moderate temperatures, i.e., $T\sim\frac{1}{10}\Theta$, owing to possible dispersion effects.

---

[1]T. H. K. Barron, A. J. Leadbetter, and J. A. Morrison, Proc. Roy. Soc. (London) A279, 62 (1964).

[2]We have also considered Ag and Au in this regard, but have found that a detailed analysis of $\gamma_l(T)$ seemed unwarranted for these metals, principally because of uncertainties in the thermal-expansion data.

[3]T. H. K. Barron and R. W. Munn, Phil. Mag. 15, 85 (1967).

[4]P. K. Sharma and N. Singh, Phys. Rev. B 1, 4635 (1970).

[5]L. Chéveau, Phys. Rev. 169, 496 (1968).

[6]E. C. Svensson, B. N. Brockhouse, and J. M. Rowe, Phys. Rev. 155, 619 (1967).

[7]R. M. Nicklow, G. Gilat, H. G. Smith, L. J. Raubenheimer, and M. K. Wilkinson, Phys. Rev. 164, 922 (1967).

[8]W. A. Kamitakahara and B. N. Brockhouse, Phys. Letters 29A, 639 (1969).

[9]The lattice parameter and elastic constants are also needed in this evaluation of the volume derivatives of the force constants.

[10]W. B. Daniels and C. S. Smith, Phys. Rev. 111, 713 (1958).

[11]Y. Hiki and A. V. Granato, Phys. Rev. 144, 411 (1966).

[12]K. Salama and G. A. Alers, Phys. Rev. 161, 673 (1967).

[13]P. S. Ho, J. P. Poirier, and A. L. Ruoff, Phys. Status Solidi 35, 1017 (1969).

[14]Y. Hiki, J. F. Thomas, Jr., and A. V. Granato, Phys. Rev. 153, 764 (1967).

[15]In the case of Cu the data of Salama and Alers (Ref.

12) correspond to a strong temperature dependence of dc_{ij}/dP. However, as pointed out by these authors, large uncertainties are associated with their results, because they did not perform hydrostatic measurements.

[16]A. K. Singh and P. K. Sharma, Phys. Status Solidi 28, 643 (1968).

[17]R. P. Gupta, P. K. Sharma, and S. Pal, Phys. Status Solidi 18, 119 (1966), and references therein.

[18]T. H. K. Barron, Phil. Mag. 46, 720 (1955).

[19]Expressions for the limits of $\gamma_D(n)$ as n approaches -3 and 0 can be found in Ref. 18.

[20]See Ref. 1; we did not employ the Euler expansions discussed in this reference.

[21]A. A. Maradudin, P. A. Flinn, and R. A. Coldwell-Horsfall, Ann. Phys. (N. Y.) 15, 337 (1961).

[22]R. H. Carr, R. D. McCammon, and G. K. White, Proc. Roy. Soc. (London) A280, 72 (1964).

[23]J. F. Kos and J. L. G. Lamarche, Can. J. Phys. 47, 2509 (1969).

[24]T. Rubin, H. W. Altman, and H. L. Johnston, J. Am. Chem. Soc. 76, 5289 (1954).

[25]D. Biji and H. Pullan, Physica 21, 285 (1955).

[26]R. O. Simmons and R. W. Balluffi, Phys. Rev. 108, 278 (1957).

[27]I. E. Leksina and S. I. Novikova, Fiz. Tverd. Tela 5, 1094 (1963) [Soviet Phys. Solid State 5, 798 (1963)].

[28]W. C. Overton and J. Gaffney, Phys. Rev. 98, 969 (1955).

[29]G. T. Furukawa, W. G. Saba, and M. L. Reilly, Natl. Bur. Std. (U.S.) Ref. Data Ser. 18 (1968).

[30]T. H. K. Barron, A. J. Leadbetter, J. A. Morrison, and L. S. Salter, Inelastic Scattering Neutrons Solids Liquids Proc. Symp. 2nd Chalk River Can. 1, 49 (1963).

[31]D. B. Fraser and A. C. Hollis-Hallett, Can. J. Phys. 43, 193 (1965).

[32]N. Waterhouse and B. Yates, Cryogenics 8, 267 (1968).

[33]J. R. Neighbours and G. A. Alers, Phys. Rev. 111, 707 (1958).

PHYSICAL REVIEW B VOLUME 3, NUMBER 6 15 MARCH 1971

X-Ray Study of the Debye-Waller Factor of Nb_3Sn†

L. J. Vieland
RCA Laboratories, Princeton, New Jersey 08540
(Received 21 August 1970)

The Debye-Waller (DW) factors for Nb and Sn atoms in the intermetallic compound Nb_3Sn have been determined by x-ray intensity measurements on a single crystal. The results are found to be in satisfactory agreement with the theory for both the angular and temperature dependence of the scattering. The data can be fitted by assigning Debye temperatures of 318 °K and 262 °K to the Nb and Sn atoms, respectively. We are unable to confirm the anomalously large value of the DW factor found in a Mössbauer-effect study.

INTRODUCTION

Nb_3Sn undergoes a phase transition from cubic to tetragonal symmetry at temperatures below about 50 °K.[1] The elastic constant C_{11}-C_{12}, which represents the stiffness of the shear mode which transforms the crystal from cubic to tetragonal, is found to decrease rapidly as the temperature is lowered, approaching zero at the transformation temperature T_m.[2] Current theories[3,4] attribute the elastic softening to a Jahn-Teller–like mechanism, in which the d-band degeneracy at the Fermi level arising from independent sub-bands associated with the three orthogonal Nb atom chains in the β-W structure, is removed by the tetragonal distortion. In this model the free-energy difference between the cubic and tetragonal states is a function of the strain alone, and the transformation is first order. Since no evidence of a first-order transformation has been observed,[5] the early suggestion that some other order parameter besides the strain might be necessary in the expansion of the free-energy difference near T_m[6] appears compelling. By analogy with certain ferroelectric transitions, the second parameter might be an optical-mode coordinate. In this case, the soft elastic mode appears as a consequence of the interaction of the low-frequency optical mode with the acoustic branch of the phonon spectrum.

Some evidence for such a mechanism was found in a study of the Mössbauer effect in Nb_3Sn.[7] It was observed that the recoil-free fraction was anomalously low, corresponding to a Debye temperature of 56 °K at 4.2 °K, and indicative of a large anharmonic contribution to the binding energy. The data could be represented as a combination of a Debye-like spectrum with reasonable $\Theta = 290$ °K, and a temperature-independent opticallike mode, which was interpreted as arising from the loose (square-well) binding of the Sn atoms. (Sn^{119} was the γ-ray source.) However, no evidence of unusual softness in the phonon spectrum has been observed in other measurements (e.g., specific heat,[5,8] and resistivity[4]). Since crystals large