Large Vibrational Effects upon Calculated Phase Boundaries in Al-Sc

V. Ozoliņš
Sandia National Laboratories, MS 9161, P.O. Box 969, Livermore, California 94551-0969

M. Asta
Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208-3108

(Received 15 June 2000)

The fcc portion of the Al-Sc phase diagram is calculated from first principles including contributions to alloy free energies associated with ionic vibrations. It is found that vibrational entropy accounts for a 27-fold increase in the calculated solubility limits for Sc in fcc Al at high temperatures, bringing calculated and measured values into very good agreement. The present work gives a clear example demonstrating a large effect of vibrational entropy upon calculated phase boundaries in substitutional alloys.

DOI: 10.1103/PhysRevLett.86.448 PACS numbers: 64.70.Kb, 63.20.–e, 64.75.+g, 65.20.+w

In the past fifteen years considerable effort has been devoted towards the development of methods for calculating composition-temperature (c-T) phase diagrams from first principles [1–3]. Until recently, contributions to alloy free energies associated with ionic vibrations were thought to be unimportant when considering the relative stability of substitutional alloy phases based upon the same underlying lattice structure. Evidence to the contrary was provided in recent experimental measurements [4] of the vibrational entropy difference (ΔS_{vib}) between long-range ordered and disordered phases for fcc-based Ni_3Al and Cu_3Au, and bcc-based Fe_3Al. These measurements produced values of ΔS_{vib} which are substantial fractions of the maximum configurational entropy difference between ordered and disordered phases at an A_3B composition, and it has been concluded that vibrational entropy may have large effects upon calculated order-disorder transition temperatures. However, in the existing theoretical first-principles calculations [5,6] a large effect of ionic vibrations upon calculated alloy phase diagrams has not yet been demonstrated.

Almost all previous studies have focused on vibrational entropy differences between phases at the same composition. The vibrational entropy difference between two phases at different concentrations, which influences the compositional range of stability of a phase, has not yet been studied in detail. In the present work, vibrational free energy contributions have been incorporated in the calculation of the phase diagram for fcc-based phases in the Al-Sc alloy system. It is found that *vibrational contributions give rise to a 27-fold increase in the calculated solubility limits for Sc in fcc Al,* ultimately resulting in a very good level of agreement between measurements and calculated results. The present study gives the first clear demonstration of a significant effect of vibrational entropy upon first-principles calculated phase boundaries in a substitutional alloy.

For Al-rich compositions the solid-state portion of the Al-Sc phase diagram features two fcc-based phases with extremely narrow phase fields [7]. The fcc-based Al solid-solution phase extends to roughly 0.2 at. % Sc at the measured eutectic temperature of 933 K. For more concentrated compositions a large two-phase field exists between the Al solid-solution phase and the ordered Al_3Sc compound possessing an fcc-based $L1_2$ (Cu_3Au-prototype) crystal structure. The filled symbols in Fig. 1 represent values for the solubility limits of Sc in fcc Al obtained from five separate resistivity measurements (see references in [7,8]). In a previous first-principles study based upon the cluster-expansion method [2,3], Asta, Foiles, and Quong found that to a very high degree of accuracy the

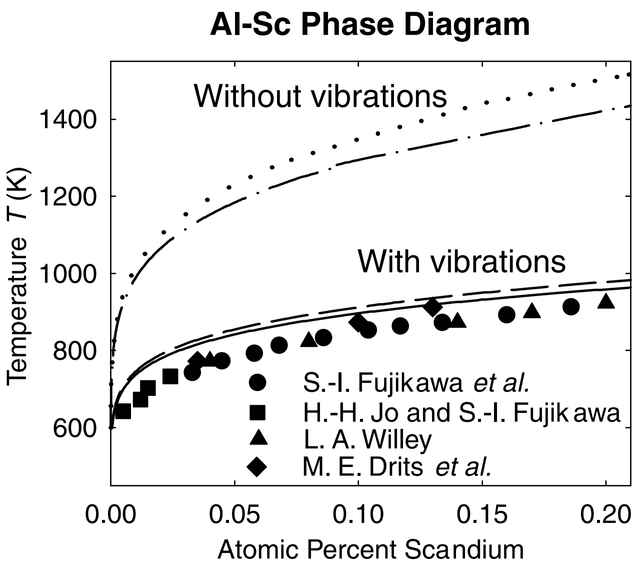

FIG. 1. Measured (symbols), and first-principles-calculated Al-rich solvus boundaries for Al-Sc alloys. Dotted and dot-dashed lines correspond to calculations with $T = 0$ K energies and $T > 0$ K electronic free energies, respectively, neglecting vibrational effects. Solid and dashed lines are calculated results including vibrational entropy in the harmonic and quasiharmonic approximations, respectively.

temperature dependent solubility limit $c_s(T)$ of Sc in fcc Al is given by the ideal solution formula:

$$c_s(T) = \exp\left[\frac{4\Delta G(\mathrm{Al_3Sc}) - \Delta G(\mathrm{Sc})}{k_B T}\right], \qquad (1)$$

where $\Delta G(\mathrm{Al_3Sc})$ is the formation value of the Gibbs free energy per atom for $\mathrm{Al_3Sc}$ and $\Delta G(\mathrm{Sc})$ is the solution free energy for a dilute Sc atom in fcc Al, expressed per Sc atom. Configurational entropy contributions are excluded from the free energies in Eq. (1), which depend only on formation enthalpies ΔH and nonconfigurational entropies ΔS_{nc} associated with vibrational and electronic free energy contributions: $\Delta G = \Delta H - T\Delta S_{\mathrm{nc}}$. If vibrational and electronic contributions to alloy free energies are neglected, the calculated [8,9] phase boundaries underestimate the measured solubility limits for Sc in fcc Al by a factor of 30, as plotted by a dotted line in Fig. 1.

To obtain the free energies in Eq. (1) we have used first-principles linear response theory [10] and the local-density approximation (LDA) to calculate harmonic phonon dispersions of ordered $\mathrm{Al_3Sc}$ and a set of supercells representing Sc impurities in fcc Al. Our calculations employ the plane-wave basis set and optimized norm-conserving pseudopotentials with multiple nonlocal projectors [11]. The Sc pseudopotential was constructed to treat semicore $3s$ and $3p$ states as valence, since these states are fairly extended and have a significant effect on the calculated specific volumes of Sc impurities. Interatomic force constants were extracted via Fourier synthesis from the directly calculated dynamical matrices. Numerical convergence was ensured by using equivalent [12] reciprocal space grids for both phonon and electron states. Phonon mode Grüneisen parameters, $\gamma_{\mathbf{q}n} = -\frac{d\ln\omega_{\mathbf{q}n}}{d\ln V}$, were obtained by taking differences of frequencies $\omega_{\mathbf{q}n}$ at two volumes separated by $\approx 4\%$.

The main results of this paper are summarized in Table I, which gives the calculated structural, elastic, and quasiharmonic vibrational properties of the studied Al-Sc compounds. We considered fcc Al, fcc and hcp Sc, ordered $L1_2$ ($\mathrm{Al_3Sc}$) compound, and several fcc-based impurity supercells: a cubic 32-atom cell ($\mathrm{Al_{31}Sc}$), a 27-atom $3 \times 3 \times 3$ cell ($\mathrm{Al_{26}Sc}$), and a 64-atom $4 \times 4 \times 4$ cell ($\mathrm{Al_{63}Sc}$). We find that the ordered $\mathrm{Al_3Sc}$ compound has a very large negative vibrational excess entropy, $\Delta S_{\mathrm{vib}}(\mathrm{Al_3Sc}) = -0.7 k_B$ atom^{-1}. In contrast, the Sc impurity in fcc Al is predicted to exhibit a slightly positive excess vibrational entropy. In the following discussion we adopt the value calculated for the $3 \times 3 \times 3$ impurity supercell, $\Delta S_{\mathrm{vib}}(\mathrm{Sc}) = +0.50\ k_B/\mathrm{Sc}$, since thermal expansion and force constants were calculated for this case only. Entropy per Sc impurity, $\Delta S_{\mathrm{vib}}(\mathrm{Sc})$, seems to be converged to within $0.15\ k_B/\mathrm{Sc}$, as seen from the difference in vibrational entropies between the $3 \times 3 \times 3$ and $4 \times 4 \times 4$ supercells. We obtain for the difference in excess entropies per Sc atom a value of $\Delta S_{\mathrm{vib}}(\mathrm{Sc}) - 4\Delta S_{\mathrm{vib}}(\mathrm{Al_3Sc}) = +3.3\ k_B$, which gives a 27-fold increase in the calculated solubility of Sc in Al. The solid line in Fig. 1 shows the effect of the harmonic vibrational entropy on the calculated solubility limit. We see that inclusion of vibrational effects dramatically improves the theoretically calculated $c_s(T)$ and brings the calculated and measured solubility limits in excellent agreement with each other. Uncertainty in $\Delta S_{\mathrm{vib}}(\mathrm{Sc})$ due to cell size will affect solubility $c_s(T)$ by a relatively small amount ($\approx 15\%$). Thermal expansion decreases solubility slightly, as shown by the dash-dotted line in Fig. 1.

Structural differences in vibrational entropy are typically attributed to changes in the number of unlike-atom nearest-neighbor (NN) bonds. It is generally expected that in strongly compound-forming systems (like Al-Sc) unlike-atom bonds are stiffer than like-atom bonds, leading to higher phonon frequencies and lower vibrational entropies. As shown previously [13], hybridization between Sc d- and Al p- electron states is very strong, and as a result, stiff NN bonds between NN, Al, and Sc are expected. To examine this idea further, in Table II we list the calculated NN bond lengths and longitudinal force constants in the $3 \times 3 \times 3$ Sc impurity supercell and in ordered $\mathrm{Al_3Sc}$. In both structures the Al-Sc bond length is well below the average of Al-Al and Sc-Sc equilibrium bond lengths, and the Al-Sc longitudinal force constants are almost twice stiffer than those for either Al-Al or Sc-Sc. Thus, our data seem to support the intuitive

TABLE I. Calculated equilibrium volumes per atom V_0, excess volumes per Sc atom $\Delta V(\mathrm{Sc})$, bulk moduli B_0, vibrational excess entropies ΔS_{vib}, average Grüneisen parameters γ_{G}, high-temperature coefficients of volume thermal expansion $\beta = \frac{1}{V}(\frac{\partial V}{\partial T})_p$, and rates of entropy increase due to thermal expansion, $(\frac{\partial S}{\partial V})_T(\frac{\partial V}{\partial T})_p$. Numbers in parentheses represent experimental values [14].

Compound	V_0 (Å^3)	$\Delta V(\mathrm{Sc})$ (Å^3)	B_0 (GPa)	ΔS_{vib} (k_B/atom)	$(\frac{\partial S}{\partial V})_T(\frac{\partial V}{\partial T})_p$ ($10^{-4}k_B$ K^{-1} atom^{-1})	γ_{G}	β (10^{-6} K^{-1})
FCC Al	15.57(16.61)		85(72)	0.00	4.2	2.12	66(69)
$\mathrm{Al_{31}Sc}$	15.76	21.6	85	+0.15[a]	⋯	⋯	⋯
$\mathrm{Al_{26}Sc}$	15.83	22.6	85	+0.50[a]	3.7[a]	2.00	62
$\mathrm{Al_{63}Sc}$	15.67	22.2	85	+0.36[a]	⋯	⋯	⋯
$L1_2$ $\mathrm{Al_3Sc}$	16.10	17.7	96	−0.70	2.1	1.60	43
FCC Sc	21.77	21.8	58	+0.12	0.9	0.93	31
HCP Sc	22.09(25.0)	22.1	61(44)	0.00	0.4	0.69	21(30)

[a] The calculated excess vibrational entropies of Sc impurities have been expressed in units of k_B/Sc atom.

TABLE II. Comparison of bond lengths d (in Å) and longitudinal force constants Φ_l (in eV/Å^2) in the studied Al-Sc compounds.

Property	fcc Al	hcp Sc	Sc impurity	$L1_2$ (Al_3Sc)
d(Al-Sc)			2.833	2.834
d(Al-Al)	2.803		2.833[a]	2.834[a]
d(Sc-Sc)		3.086		
Φ_l(Al-Sc)			−2.32	−2.05
Φ_l(Al-Al)	−1.36		−1.08[a]	−1.12[a]
Φ_l(Sc-Sc)		−1.29		
ΔV(Sc)		22.1 Å^3/Sc	22.6 Å^3/Sc	17.7 Å^3/Sc
ΔS_{vib}(Sc)			+0.5 k_B/Sc	−2.8 k_B/Sc

[a] Both Al atoms share a nearest-neighbor Sc atom.

picture where low vibrational entropy of the ordered Al_3Sc structure is due to strong unlike-atom bonds. However, a puzzling question emerges from comparing the data in Table II: Why is the vibrational entropy of formation per Sc atom strongly negative for ordered Al_3Sc [$4\Delta S_{\mathrm{vib}}(Al_3Sc) = -2.8\ k_B/\mathrm{Sc}$], but slightly positive for the Sc impurity in fcc Al [$\Delta S_{\mathrm{vib}}(\mathrm{Sc}) = +0.5\ k_B/\mathrm{Sc}$]? Indeed, in both cases each Sc atom has twelve NN-Al atoms and, furthermore, the Al-Sc longitudinal force constant is ≈10% stiffer in the impurity case than in ordered Al_3Sc. The change of sign of ΔS_{vib} is in stark contrast with expectations based on the intuitive picture described above. To understand this paradox, we examine each case separately and show that considerations based on the number of NN bonds have to be used with caution.

Ordered Al_3Sc.—Figure 2 shows the calculated phonon density of states (DOS) for ordered Al_3Sc. We also show in Fig. 2 the "excess phonon DOS" $\Delta g(\omega)$ for Al_3Sc, obtained by subtracting composition-weighted phonon DOS of the constituents. As is evident from $\Delta g(\omega)$, ordered Al_3Sc has higher average phonon frequencies and less weight in the low-frequency region compared to fcc Al and hcp Sc. Since the harmonic vibrational entropy at $k_BT \gg \hbar\omega_{\max}$ is proportional to the logarithmic moment of phonon DOS, the entropy of formation ΔS_{vib} is determined by $\Delta g(\omega)$: $\Delta S_{\mathrm{vib}} = k_B \int_0^{\omega_{\max}} \ln(\frac{k_BT}{\hbar\omega})\Delta g(\omega)\,d\omega$. Because of well-known properties of logarithm, low frequencies are weighed more heavily in ΔS_{vib}. We conclude that the large negative value of $\Delta S_{\mathrm{vib}}(Al_3Sc)$ is determined by low phonon DOS in the acoustic region, which in turn can be attributed to pronounced stiffening of elastic constants of ordered Al_3Sc.

Sc impurity in fcc Al.—From Table I we see that the excess volume per Sc impurity, ΔV(Sc), roughly obeys Vegard's law. However, Table II shows that the equilibrium Al-Sc bond length is almost the same as in ordered Al_3Sc ($d = 2.833$ Å). This is geometrically possible only if farther-neighbor shells around the Sc impurity expand to accommodate the Vegard's law. This expansion lowers restoring forces on Al atoms in these shells, causing an increase in $\Delta S_{\mathrm{vib}}(\mathrm{Sc})$ that offsets the decrease due to existence of 12 very stiff NN Al-Sc bonds around the impurity [see Φ_l(Al-Sc) in Table II]. This idea can be made more quantitative by considering atom-decomposed partial excess entropies, defined in analogy with atom-decomposed partial phonon DOS:

$$\Delta S_{\mathrm{vib}}(i) = \sum_{\mathbf{q}n} |\mathbf{e}_i(\mathbf{q}n)|^2 S\left(\frac{\hbar\omega_{\mathbf{q}n}}{2k_BT}\right) - S_{\mathrm{vib}}^{\mathrm{bulk}}(i), \quad (2)$$

where i labels atoms, $S(x) = x/\tanh(x) - \ln[2\sinh(x)]$ is the harmonic phonon mode entropy function, and $S_{\mathrm{vib}}^{\mathrm{bulk}}(i)$ is vibrational entropy of pure bulk constituent i. The total excess entropy per Sc atom is then given by $\Delta S_{\mathrm{vib}}(\mathrm{Sc}) = \sum_i \Delta S_{\mathrm{vib}}(i)$. Figure 3(a) shows the calculated $\Delta S_{\mathrm{vib}}(i)$ obtained from the $4 \times 4 \times 4$ impurity supercell. It is seen that the Sc atom has the most negative $\Delta S_{\mathrm{vib}}(i)$, which is a consequence of the fact that the Al-Sc bonds are much stiffer than Sc-Sc bonds in hcp Sc (see Table II). The nearest-neighbor Al shell shows a slightly negative $\Delta S_{\mathrm{vib}}(i)$, but the surrounding shells all contribute

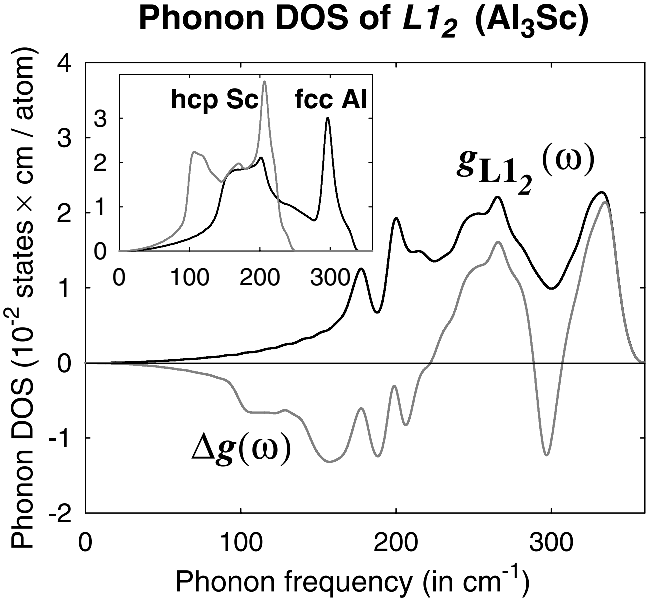

FIG. 2. Calculated phonon DOS for ordered Al_3Sc. The lower curve represents $\Delta g(\omega) = g_{L1_2}(\omega) - \frac{3}{4}g_{\mathrm{Al}}(\omega) - \frac{1}{4}g_{\mathrm{Sc}}(\omega)$. The inset shows the calculated phonon DOS of fcc Al and hcp Sc.

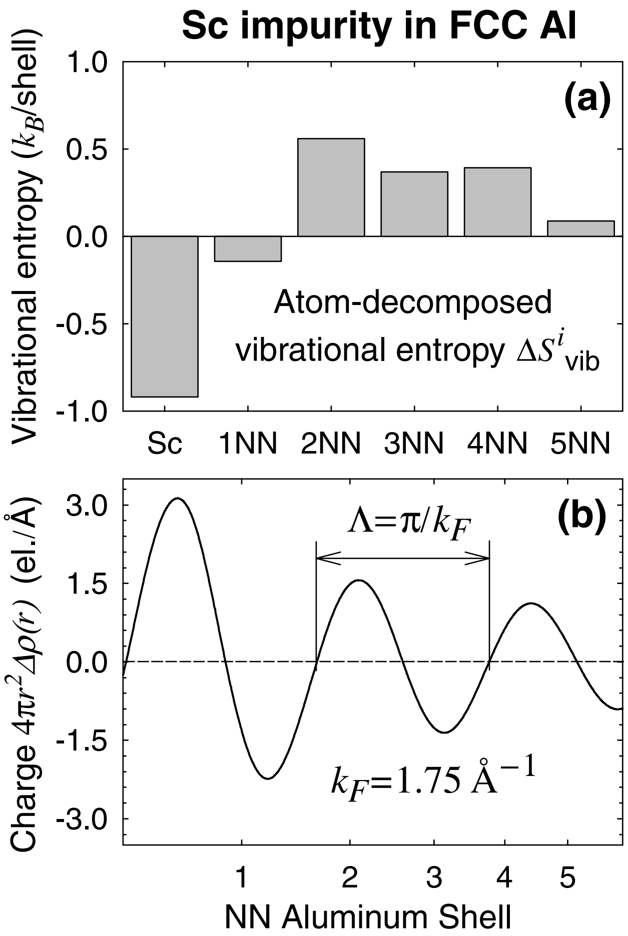

FIG. 3. (a) Atom-decomposed excess vibrational entropies $\Delta S_{\text{vib}}(i)$ [see Eq. (2)]. (b) Spherically averaged charge density perturbation $4\pi r^2 \Delta\rho(r)$ around a Sc impurity in fcc Al.

positive excess entropies, leading to a slightly positive net value of $\Delta S_{\text{vib}}(\text{Sc}) = +0.36\ k_B/\text{atom}$. The largest positive value of $\Delta S_{\text{vib}}(i)$ per atom is found for the 2NN shell [$\Delta S_{\text{vib}}(2) = +0.1\ k_B/\text{Al}$].

Two conceptually distinct effects contribute to the "softening" of farther-neighbor Al shells around a Sc impurity: (i) geometric volume expansion discussed in the previous paragraph, and (ii) electronic Friedel oscillations associated with the Sc impurity. Both (i) and (ii) are physically intertwined, and it is difficult to meaningfully isolate their effect on the phonon dispersion. An order-of-magnitude estimate of contribution to $\Delta S_{\text{vib}}(\text{Sc})$ from the first effect can be obtained in the following manner: using the relation $(\frac{\partial S}{\partial V})_T = \gamma_G C_V/V$ and taking the difference between $\Delta V(\text{Sc})$ in Al_{63}Sc and ordered Al_3Sc, $\delta V = 4.7$ Å^3, we find $\Delta S = (\frac{\partial S}{\partial V})_T \delta V = +1.9\ k_B/\text{Sc}$. While obviously an oversimplification, this estimate shows that the volume effect can be very large. Regarding the second effect, we find a net charge transfer of $\approx$0.3 electrons to the Sc impurity and the surrounding twelve NN-Al atoms. This charge transfer is a consequence of the strong hybridization lowering the energy of the p-d bonding states between Al and Sc. In Fig. 3(b) we show the resulting Friedel oscillations around a Sc impurity, calculated as a spherical average of the difference between total charge densities of 128-atom supercells of fcc Al with and without the Sc impurity at $\mathbf{R} = 0$, holding all Al atoms fixed. We find that the resulting changes in electronic charge density are of the same magnitude as those due to volume expansion, and they should therefore have comparable effects on the interatomic force constants.

In conclusion, we have demonstrated that inclusion of vibrational entropy is crucial for calculating the solvus boundary in Al-Sc. Our analysis reveals that NN-bond counting arguments are insufficient to explain the influence of vibrational effects on the Al-Sc phase diagram. Rather, we find that longer-ranged effects play a major role: Sc impurities induce perturbations in farther-neighbor Al shells that act to cancel out the vibrational entropy decrease from stiff NN Al-Sc bonds.

This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Materials Science Division, under Contract No. DE-AC04-94AL85000.

[1] F. Ducastelle, *Order and Phase Stability in Alloys* (North-Holland, New York, 1991).

[2] D. de Fontaine, Solid State Phys. **47**, 33 (1994).

[3] A. Zunger, in *Statics and Dynamics of Alloy Phase Transformations,* edited by P. E. A. Turchi and A. Gonis, NATO Advanced Study Institutes, Ser. B, Vol. 319 (Plenum, New York, 1994).

[4] L. Anthony *et al.,* Phys. Rev. Lett. **70**, 1128 (1993); B. Fultz *et al.,* Phys. Rev. B **52**, 3315 (1995); L. J. Nagel *et al.,* Philos. Mag. Lett. **72**, 421 (1995); L. Anthony *et al.,* Phys. Rev. Lett. **73**, 3034 (1994).

[5] A. van de Walle, G. Ceder, and U. V. Waghmare, Phys. Rev. Lett. **80**, 4911 (1998); A. van de Walle and G. Ceder, Phys. Rev. B **61**, 5972 (2000).

[6] V. Ozoliņš, C. Wolverton, and A. Zunger, Phys. Rev. B **58**, R5897 (1998).

[7] G. Cacciamani *et al.,* Intermetallics **7**, 101 (1999).

[8] M. Asta, S. M. Foiles, and A. A. Quong, Phys. Rev. B **57**, 11 265 (1998).

[9] M. Asta and V. Ozoliņš (unpublished)

[10] S. Baroni *et al.,* Phys. Rev. Lett. **58**, 1861 (1987).

[11] A. Rappe *et al.,* Phys. Rev. B **41**, 1227 (1990); D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990); For Al, we used the nonlinear core correction of S. Louie *et al.,* Phys. Rev. B **26**, 1738 (1982).

[12] S. Froyen, Phys. Rev. B **39**, 3168 (1989). Electron and phonon states of hcp Sc were sampled on 18 × 18 × 12 and 9 × 9 × 6 grids, respectively.

[13] A. E. Carlsson and P. J. Meschter, J. Mater. Res. **4**, 1060 (1989).

[14] *American Institute of Physics Handbook,* edited by D. E. Gray (McGraw-Hill, New York, 1972); *Thermal Expansion,* edited by Y. S. Touloukian *et al.* (Plenum, New York, 1975).