Anharmonic Effects in the *A*15 Compounds Induced by Sublattice Distortions

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We demonstrate that elastic anomalies and lattice instabilities in the *A*15 compounds are describable in terms of first-principles local density approximation electronic structure calculations. We show that at $T = 0$ V_3Si, V_3Ge, and Nb_3Sn are intrinsically unstable against shears with elastic moduli $C_{11} - C_{12}$ and C_{44}, and that the zone center phonons, Γ_2 and Γ_{12}, are either unstable or extremely soft. We demonstrate that sublattice relaxation (internal strain) effects are key to understanding the behavior of the *A*15 materials. [S0031-9007(97)03837-4]

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The *A*15 materials have been of interest for more than 40 years due to the relatively high superconducting transition temperatures for many of them and the interplay between their superconductivity, their structural phase transitions, and their temperature-dependent anomalies in properties such as elastic constants, phonon spectra, electrical resistivity, Knight shift, and magnetic susceptibility [1–3]. The paradigm interesting *A*15 materials are V_3Si and Nb_3Sn, both of which have relatively high T_c values and also undergo cubic-to-tetragonal structural phase transitions just above T_c (with $\frac{c}{a} > 1$ and $\frac{c}{a} < 1$, respectively; see Fig. 1), and have many other anomalous properties as well. Many theoretical models, discussed in Refs. [1–3], attempt to explain the unusual properties of the *A*15 materials in terms of models with a sharply peaked structure in the electronic density of states (DOS) near the Fermi level, E_F.

Although the past ten years have seen a major focus on developing an understanding of the ceramic oxide superconductors [4], there remain many unanswered fundamental questions related to the unusual properties of the *A*15 materials, including the question of the relationship between their high T_c and their structural anomalies or instabilities, and whether or not they are driven directly by the electronic distribution using a conventional Fermi liquid description of the electronic structure, or whether "exotic" excitations are needed to explain the properties. Some of these issues may have relevance to the high T_c oxides as well, where structural instabilities are also known to exist [4].

Here we show that using state-of-the-art first-principles electronic structure methods to study three of the most interesting *A*15 materials: V_3Si, Nb_3Sn, and V_3Ge. We have found several provocative results, including the facts that (1) for all three materials the calculated elastic constants agree very well with the observed room temperature values if sublattice relaxation effects are frozen out; (2) when sublattice relaxation effects are included, the crystals are unstable in the cubic *A*15 structure with respect to a tetragonal distortion which stabilizes both the elastic constants and the phonon anomalies; (3) the structural instability is weakest (in terms of the energetics) in V_3Ge and may not be observable due to effects of crystal imperfections; (4) anomalies in several of the zone-center phonon branches occur along with the elastic anomalies, the branches corresponding to modes where atoms in the chains vibrate in the chain direction.

The electronic structure results reported in this Letter were generated using the all-electron, full-potential linearized-augmented-plane-wave (LAPW) method in the local density approximation (LDA). The valence or conduction band states were treated semirelativistically (no spin-orbit effects) while the core states were treated fully relativistically. Care was taken to ensure appropriate *k*-point convergence for the accuracy needed in these studies.

Usually it is found that the elastic constants, *when evaluated at the experimental volume,* are within (5–10)% of the experimental values [5]. For a cubic system (such as the *A*15) to be mechanically stable, the bulk modulus ($B \equiv \frac{C_{11}+2C_{12}}{3}$) and shear elastic constants ($C_{11} - C_{12}$ and C_{44}) must be positive. The overall phonon spectrum must be stable as well (positive square frequencies). The elastic constants can be extracted using the procedures discussed by Mehl *et al.* [5]: (i) calculate the total energy

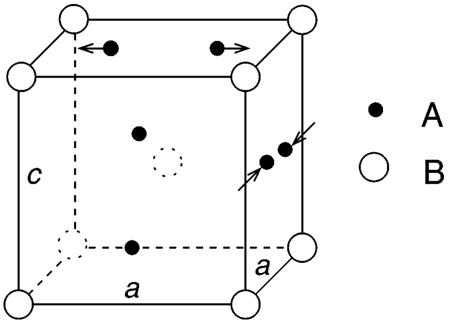

FIG. 1. Schematic diagram of ideal ($c = a$) and tetragonally distorted ($c \neq a$) *A*15 crystal structures (A_6B_2). *B* atoms form a body-centered cube, while *A* atoms form linear chains on each cube face. Arrows denote allowed internal degrees of freedom (direction of sublattice relaxations) in the tetragonally distorted *A*15 structure.

as a function of the volume, and then fit the results to an equation of state to extract the bulk modulus B; (ii) apply an appropriate strain to the lattice to distort the primitive lattice vectors, calculate the total energy versus strain δ at volume V, and determine the second-order elastic constants from the coefficient second order in the strain. For example, using an orthorhombic distortion, the distortion energy is

$$\Delta E(\pm\delta) = V(C_{11} - C_{12})\delta^2 + O(\delta^4). \quad (1)$$

We can thus extract $C_{11} - C_{12}$ from Eq. (1). Similarly, we used a monoclinic distortion to extract C_{44}.

Our calculated total energies of V_3Si, V_3Ge, and Nb_3Sn in the $A15$ structure as a function of volume were used to extract the equilibrium volumes and bulk moduli of these materials. The calculated equilibrium volumes are underestimated by (4–6)%, typical of LDA calculations, leading to the calculated equilibrium bulk moduli being overestimated compared to experiment by more than $\sim$25%. On the other hand, the calculated bulk moduli at the *experimental volumes* are very close ($\sim$5%) to those of experiment, as shown in Table I.

Next, we examined the stability of the $A15$ materials under the application of shears corresponding to the elastic constants $C_{11} - C_{12}$ and C_{44}, first without allowing the cell-internal sublattice displacements that are allowed by the broken symmetries produced by the elastic distortions. Figure 2 depicts our calculated distortion energies (open squares) as a function of δ^2 using orthorhombically distorted cells. For a perfectly harmonic crystal, the data points would fall on a straight line, with the slopes given by $C_{11} - C_{12}$. Indeed the calculated points fall quite close to straight lines, indicating only small contributions from higher order terms $[O(\delta^4)]$. The fitted $C_{11} - C_{12}$ and C_{44} values, shown in Table I, are very close to the experimental room temperature values, rather than to the low temperature values as might be expected for a typical material. Since first-principles calculations are supposed to correspond to $T = 0$, not to high temperatures, why do we not reproduce the soft elastic constants seen at low temperature?

This puzzle was solved by realizing that as one distorts a crystal from a higher to a lower symmetry space group, new internal degrees of freedom could be introduced with significant physical and computational importance, especially for systems with lattice instabilities. We note that it is tempting to overlook these sublattice distortions because determining their effect introduces a large increase in the computational burden, since for each internal distortion a set of self-consistent calculations needs to be performed to find the equilibrium sublattice distortions corresponding to the volume and strain under investigation.

For the orthorhombically distorted $A15$ cell, the sublattice displacements correspond to pairs of A atoms moving toward or away from each other (rather than fixing on their symmetry mandated $A15$ positions), but different pairs move independently. Thus, we need to add (iii) sublattice relaxation into our above procedures for calculating elastic constants. After fully relaxing the sublattices, we have found that the relaxed distortion energies for the $A15$ compounds (denoted by filled circles in Fig. 2) are lowered by a substantial amount, which increases as the distortion gets larger. The relaxed distortion energies show a minimum around $\delta \sim (1-2)\%$ and even dip below the energies of the "ideal" cubic $A15$ structure. Hence, these three $A15$ compounds are intrinsically unstable in the cubic structure at $T = 0$. Note that the $C_{11} - C_{12}$ instability appears to be weakest in V_3Ge. Again, the weakest C_{44} instability occurs in V_3Ge, while the strongest instability occurs for Nb_3Sn, as seen in experiment (Table I).

An alternative way to obtain $C_{11} - C_{12}$ is to distort the cell tetragonally. This tetragonally distorted cell turns out to have the same structure as the observed tetragonal phase [6] for some $A15$ compounds (Fig. 1). The distortion energies are depicted as a function of distortion ($\delta = \frac{c}{a} - 1$) in Fig. 3. If we freeze the atoms in their $A15$-like coordinates, the calculated sublattice-unrelaxed distortion energies (denoted by open squares)

TABLE I. LAPW calculated and experimental elastic constants (in GPa) (from Ref. [1]). Calculations were performed at the experimental volume using orthorhombic (for $C_{11} - C_{12}$) and monoclinic (for C_{44}) distorted cells. "Unrelaxed" refers to calculations in which atomic positions are held fixed at their cubic, ideal sites, while "relaxed" refers to calculations in which sublattices are allowed to relax. The elastic constants were extracted from a least squares fit of distortion energies to the form: $\Delta E = k_2\delta^2 + k_4\delta^4$. "Transforming" ("nontransforming") denotes an experimental sample that undergoes (does not undergo) a cubic to tetragonal phase transition. The unrelaxed $C_{11} - C_{12}$ values can also be extracted using a tetragonal distortion: such extracted values are within 6% of those reported here.

		V_3Si			V_3Ge			Nb_3Sn		
	Temp (K)	B	$\frac{c_{11}-c_{12}}{2}$	C_{44}	B	$\frac{c_{11}-c_{12}}{2}$	C_{44}	B	$\frac{c_{11}-c_{12}}{2}$	C_{44}
Calc. (unrelaxed)	0	165	84	79	169	93	77	159	91	53
Expt. (transforming)	300	176	83.8	81.0			69.8	154	68	40.8
Expt. (nontransforming)	300	171	86	80.9	170	92	70.3	160	70.7	39.6
Calc. (relaxed)	0	165	<0	<0	169	<0	<0	159	<0	<0
Expt. (transforming)	4.2	177	1.5	76.1			73.8	161	112	22.8
Expt. (nontransforming)	4.2	171	8	76.6	173	98.3	72.3	165	0	26.6

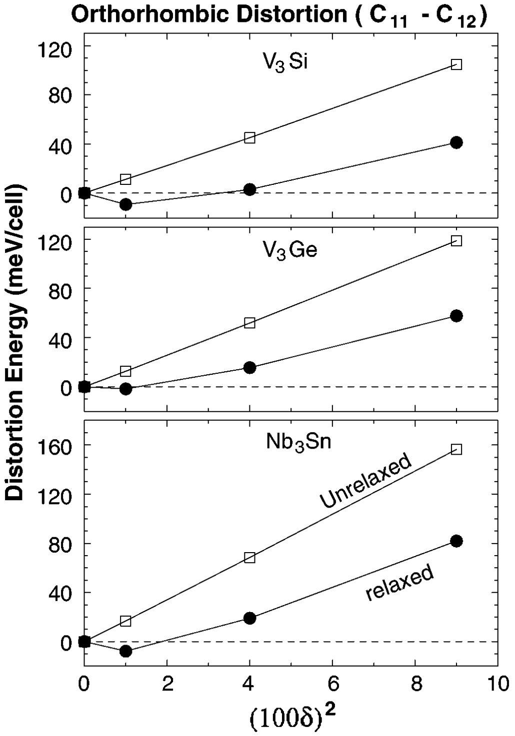

FIG. 2. Distortion energies for orthorhombically distorted *A*15 structure. Calculations were performed at the experimental *A*15 volumes. The open squares denote calculation performed with *A*15-like internal coordinates, while filled circles denote calculations with internal coordinates fully relaxed.

fall quite closely on a parabola. Note that the distortion energy contains odd terms of distortion $\delta = \frac{c}{a} - 1$ rather than being an even function of δ as in the case of orthorhombic and monoclinic distortions, so that we needed to perform more first-principles calculations (for $\pm\delta$) for this case. Indeed, we see a slight asymmetry about the $\delta = 0$ axis, indicating a small cubic term $[O(\delta^3)]$. Least-squares fitting these data to the form $a\delta^2 + b\delta^3 + c\delta^4$, we can extract $C_{11} - C_{12} = 3a/V$. Such fitted $C_{11} - C_{12}$ values are within 6% of those shown in Table I using orthorhombically distorted cells.

Next we allowed the internal coordinates to relax in a manner consistent with the tetragonal structure, and found that the distortion energies were lowered by a large amount, showing a double well structure with respect to $\frac{c}{a}$. In the case of V_3Si, the minimum occurs for $\frac{c}{a} > 1$, while for Nb_3Sn the minimum occurs for $\frac{c}{a} < 1$, in agreement with experimental observations [1]. For the case of V_3Ge, we find an extremely shallow well and a much weaker instability (bordering on the accuracy of our LAPW calculations). Therefore, a small amount of sample imperfection, such as impurities, vacancies, or disorder, or thermal effects, could inhibit the transition from occurring in V_3Ge. Experimentally, no cubic-to-tetragonal phase transition has been observed for V_3Ge, although there is some evidence for anomalies in its elastic constants [7].

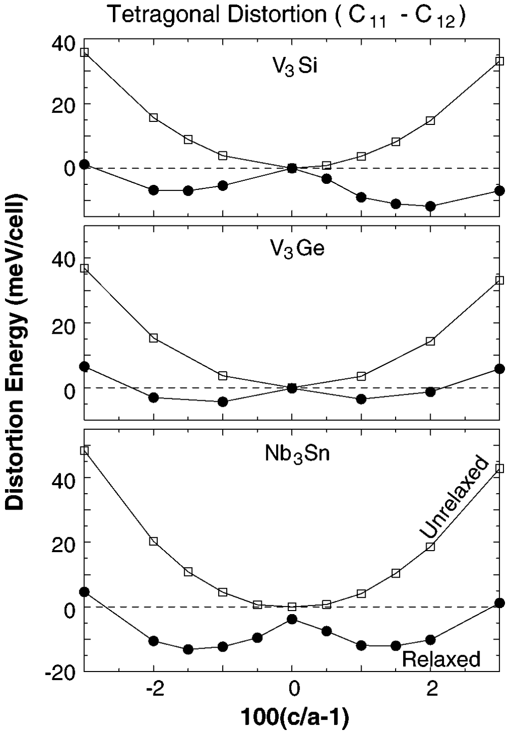

FIG. 3. Distortion energies for tetragonally distorted *A*15 structure and also see the caption of Fig. 2

For V_3Si and Nb_3Sn, the details of the structural phase transitions are very sensitive functions of sample conditions, with, for instance, the observed $\frac{c}{a}$ ratios, varying from 0.9964 to 0.9938 for Nb_3Sn and approximately 1.0024 for V_3Si [1], while the calculated minimum occurs at $\frac{c}{a}$ about 1.02 and 0.985 for V_3Si and Nb_3Sn, respectively, significantly larger than experiment. Since the relaxed distortion energy curves are very small and the curves are very flat, a precise determination of the $\frac{c}{a}$ ratio is difficult, although most of the quantitative disagreement between theory and experiment can be ascribed to LDA errors that do not affect the conclusions regarding the instabilities that we are focusing on.

We see from these results that the key to understanding the elastic constant softening, and most probably other anomalous properties in the *A*15 materials, is the relaxation of the internal degrees of freedom (sublattice relaxation) when there are cell distortions, which leads to highly anharmonic behavior in the *A*15's, general ideas put forward by Testardi [8]. At high temperatures, thermal motion washes away the well structure and atoms spend the majority of their time away from the flat well minima and assume "average" *A*15 positions. Calculations with "frozen-in" *A*15-like coordinates give the maximum attainable elastic constants, which correspond closely to the experimental room temperature values. As the temperature is lowered, the effect of sublattice relaxation sets in, and at $T = 0$, these *A*15 compounds are intrinsically unstable with respect to $C_{11} - C_{12}$ and C_{44} shear distortions.

These results can be interpreted in terms of a ferroelastic type of instability as discussed by Miller and Axe [9], with examples given in the book of Salje [10].

We have seen that the first-principles electronic structure method predicts the existence of elastic constant instabilities and the cubic to tetragonal phase transition in $A15$ materials. It is also well established that the overall phonon spectra of many of the $A15$'s exhibit unusual temperature dependencies and selected softening in different parts of the Brillouin zone [6,11,12]. Such instabilities for the phonons also follow from our calculations using the frozen phonon method which we have applied to determine the zone-center optic phonons. Note that the *relaxed* distortion energy in Fig. 3(c) for Nb_3Sn at $\delta = 0$ ($\frac{c}{a} = 1$) has a small negative value of ~ -4 meV/cell, indicating an unstable zone center Γ_{12} phonon, since this phonon has the same space group as the tetragonally distorted $A15$ cell, but with $c \equiv a$. The calculation for the Γ_2 phonon (pairs of A atoms move toward or away from each other with the same displacements for all three orthogonal chains) also shows a small, negative phonon energy for Nb_3Sn, indicating an instability. Calculations for the Γ_{12} and Γ_2 phonons for V_3Si and V_3Ge also show anomalies. However, for these materials these phonons have negative or very small positive energies; e.g., their phonon energies are less than 1 meV/cell for the Γ_{12} phonon at a displacement of $0.003a$, where a is the cubic lattice constant. For comparison, zone-center phonon energies at the same displacement for a typical intermetallic compound such as Cu_3Pt in the cubic $L1_2$ structure are ~ 25 meV/cell (where the unit cell contains 4 atoms). Note that since we estimate the accuracy of our LAPW calculations for phonon energies to be approximately 2 meV/cell, we can argue that the zone-center phonons Γ_{12} and Γ_2 are extremely soft at best, and are on the borderline of being stable or unstable.

First-principles electronic structure calculations have shown that the DOS near E_F for V_3Si and Nb_3Sn have very sharp structures [13,14], in qualitative agreement with early model calculations of the DOS, and we find similar results here. What is particularly interesting, however, is that we find explicitly that the DOS singularities, and the associated Fermi surface nesting features, are removed following the sublattice distortions and the resultant structural phase transitions. We will discuss this more fully in a future publication.

In summary, it appears that many of the unusual properties of the $A15$ materials are describable in terms of "standard" LDA electronic structure calculations when sublattice relaxation effects are included. We have shown that the $A15$ materials (V_3Si, V_3Ge, and Nb_3Sn) are intrinsically unstable against shears producing the moduli $C_{11} - C_{12}$ and C_{44}, at $T = 0$. Our calculations also indicate that the zone-center phonons (Γ_2 and Γ_{12}) are either unstable or extremely soft at $T = 0$. Similar studies of the full phonon spectrum and the superconducting tunneling functions for the $A15$ materials are being formulated to verify whether the standard LDA methods are consistent with all of the experimental data.

As a word of caution, we urge that elastic stability of a "computer-designed" novel material should always be checked, as one would not have anticipated the calculated instabilities in the $A15$ materials by examining the total energy versus volume curves alone.

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