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Brief Reports

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First-principles phonon spectra in Ca and Sr

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Experimental phonon spectra for the fcc alkaline-earth metals Ca and Sr have only recently been obtained. First-principles, generalized-pseudopotential-theory predictions of these spectra, including the full effects of *d*-state hybridization, are reported and compared with these results. The overall agreement between theory and experiment is found to be quite good (within about 10%). In addition, anomalous behavior observed in the $T_1[110]$ branch for single-crystal Ca is also found theoretically.

First-principles calculation of phonon frequencies within the general framework of the Kohn-Sham local-density-functional formalism[1] has attracted a great deal of recent attention.[2-9] Semiconductors,[2-5] simple metals,[6,8,9] and *d*-band metals[7-9] have been studied with newly developed nonperturbative pseudopotential[2-4,6,7] and LCAO (linear combination of atomic orbital)[5,7] techniques and in the case of metals with the perturbative generalized-pseudopotential theory (GPT)[8,9] as well. The nonperturbative calculations have provided a direct test of the quantitative ability of the local-density theory itself to treat phonons, and in this regard the results obtained to date are in generally excellent agreement with experiment. At the same time, such methods are of great difficulty to employ in practice, and in metals application has been limited to high-symmetry "frozen" phonons.[6,7] The alternative GPT method, on the other hand, offers for *d*-band metals the same spirit of calculation of phonons that conventional pseudopotential theory[10] does for simple metals. An arbitrary phonon frequency $\nu(\vec{q})$ can be calculated at a general wave vector $\vec{q}$ directly in terms of structure-independent characteristic functions for the metal (in general, an effective valence, an energy–wave-number characteristic, and a *d*-state overlap potential), which, in turn, can be obtained from first-principles considerations.

Quite recently,[9] optimized GPT characteristic functions have been obtained for a number of metals, including the empty-*d*-band alkaline-earth metals Ca and Sr whose phonon spectra have also been only recently measured.[11-14] We report here for the first time both the full GPT-predicted phonon spectra for Ca and Sr based on these optimized functions and direct comparisons of our results with the new experimental data. The heavy alkaline-earth metals are of special interest in these regards because they represent the simplest nontrivial subclass of *d*-band metals, with essentially unoccupied *d* states lying above but in close proximity to the Fermi level. As has been previously shown,[8,9,15-18] the band structure and physical properties of these metals are strongly influenced by the presence of the *d* states through hybridization effects at and below the Fermi level. In the prototype metals Ca and Sr, *d*-state hybridization accounts for fully one-third of the cohesive energy of the metal[9,17] and is the main driving force in establishing the observed low-temperature fcc crystal structure and the temperature-induced fcc → bcc phase transitions.[9,18] Moreover, additional interest in the role of the *d* states has been aroused by the recent prediction[16] and observation[19] of pressure-induced sequences of structural phase transitions in these elements.

The absence until now of experimental data on Ca and Sr phonons reflects in large part the historical difficulty of growing sufficiently large single-crystal samples of these metals in their low-temperature fcc phase to perform the necessary neutron scattering measurements. This, however, has at last been accomplished for Ca and a room-temperature phonon spectrum for the single-crystal metal has been reported.[11] At the same time, a new experimental analysis technique has been developed independently[13] which permits approximate determination of phonon spectra from neutron scattering data on polycrystalline samples as well. In this technique a Born–von Kármán model with finite-range interactions is assumed for the phonons and the unknown force constants are fitted to the experimental scattering data. This is justified to the extent that the dispersion curves are relatively smooth and has been demonstrated to produce accurate results in test cases.[13] Room-temperature results for both Ca and Sr have been obtained in this manner.[13,14]

We have performed optimized GPT calculations of the phonon spectra of Ca and Sr at zero temperature and the observed equilibrium atomic volumes. Our calculated results are compared with the polycrystalline data in Figs. 1 and 2, for Ca and Sr, respectively, and with the single-crystal Ca data in Fig. 3. Plotted in each case are the longi-

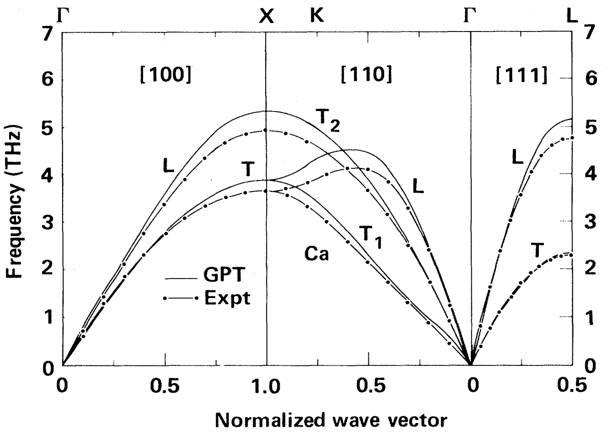

FIG. 1. Theoretical GPT phonon spectrum of fcc Ca vs the experimental results of Ref. 13 on polycrystalline material.

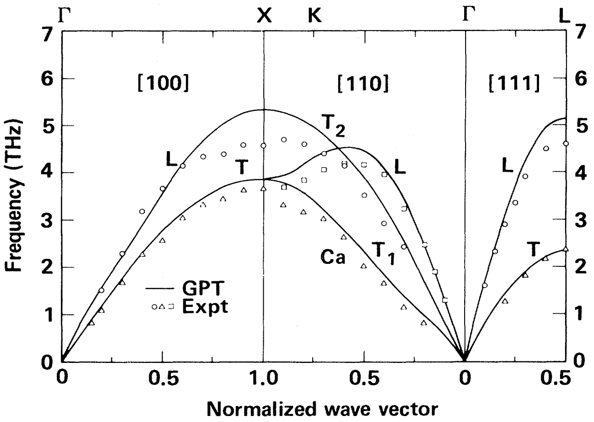

FIG. 3. Theoretical GPT phonon spectrum of fcc Ca vs the experimental results of Ref. 11 on single-crystal material.

tudinal (L) and transverse (T or T_1 and T_2) frequencies in the [100], [110], and [111] symmetry directions of the fcc Brillouin zone. The overall agreement between theory and experiment is seen to be quite good, especially in the case of the polycrystalline data where the calculated results are everywhere within about 10% of experiment. The most significant difference between the two sets of experimental Ca data lie in the high–wave-vector longitudinal [100] and [111] frequencies near the zone boundaries, with the single-crystal $\nu(\vec{q})$ somewhat lower in magnitude. The corresponding transverse branches, in contrast, are in excellent agreement with each other and with the GPT calculations.

The net effect of the *d*-state hybridization on the Ca and Sr phonon spectra is to lower the calculated frequencies, and thereby improve agreement with experiment, although this occurs in a nonuniform way with the longitudinal branches affected most strongly, as shown in Table I for Ca. In addition, the small remaining discrepancies seen in Figs. 1–3 for the high–wave-vector longitudinal frequencies appear to be explainable as a slight underestimate in the present GPT calculations of the hybridization. If the effective strength of the hybridization is increased[20] to produce optimum agreement between the GPT electron band structure and independent, self-consistent LMTO (linear muffin-tin orbital) calculations of the same,[15,21] the phonon frequencies are lowered by about the amount needed to reconcile theory and experiment. This is also demonstrated in Table I for Ca.

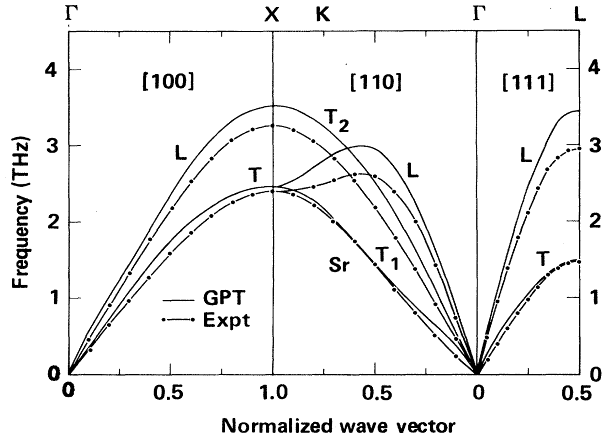

FIG. 2. Theoretical GPT phonon spectrum of fcc Sr vs the experimental results of Ref. 14 on polycrystalline material.

Our calculated phonon spectra in both Ca and Sr show evidence of weak anomalous behavior in the L[100], L[111], and T_1[110] branches. These anomalies all take the form of positive curvature inflections in the curves at intermediate wave vector, but only that in the T_1[110] branch is strong enough to be significant. This latter anomaly can also be found in the single-crystal Ca data.[11,12] The origin of this behavior is possibly related to the familiar Kohn effect,[10] but in any case, the position and nature of the positive curvature inflection are strongly influenced by the *d*-state hybridization, as shown in Fig. 4. In the absence of the hybridization, the T_1 branch begins at $\vec{q}=0$ with positive curvature and then slowly reverses to normal negative curvature behavior as $\vec{q}$ increases. With hybridization included, on the other hand, there is initially negative curvature in the T_1 branch and then a relatively strong inflection at larger $\vec{q}$, which appears to be consistent with experiment. The single-crystal Ca data also show an anomalous dip in the T_1 branch along the Brillouin-zone boundary between *K* and *X*, which is not seen in our calculations. This dip is questionable, however, because the T_1 branch by symmetry must approach the *X* point with zero slope.

Additional insight has been gained by a real-space analysis of the individual near-neighbor contributions to the Ca and Sr phonon spectra in terms of the respective central-force interatomic potentials. We find that the above anomalies are produced by very long-range forces (beyond 12th-neighbor interactions, suggestive of Kohn-type behavior), but that otherwise the basic shape and magnitude of the phonon spectra are dominated by short-range forces. The zone-boundary frequencies, in fact, are converged to within

TABLE I. GPT zone-boundary electron band energies (in Ry) and phonon frequencies (in THz) for Ca calculated in the simple-metal limit with no hybridization, in the empty-d-band–metal limit with hybridization included (Ref. 9), and in the latter limit with the d-state energy lowered by E_d^{shift} (see Ref. 20).

	GPT			LMTO[a]	Expt.	
Hybridization	No	Yes	Yes	Yes	...	
E_d^{shift}	0.0	0.0	−0.06	...	...	
Band energies						
$X_{4'}$-Γ_1	0.36	0.36	0.36	0.37		
X_1-Γ_1	0.37	0.29	0.27	0.25		
$L_{2'}$-Γ_1	0.28	0.28	0.28	0.28		
L_1-Γ_1	0.27	0.23	0.22	0.22		
Phonon frequencies						
L[100]	6.0	5.3	5.0		4.9[b]	4.5[c]
T[100]	4.0	3.9	3.7		3.6	3.6
L[111]	6.0	5.2	4.7		4.8	4.6
T[111]	2.4	2.3	2.3		2.3	2.4

[a] Reference 21. Same as Fig. 4(b) of Ref. 15.

[b] Reference 13.

[c] Reference 11.

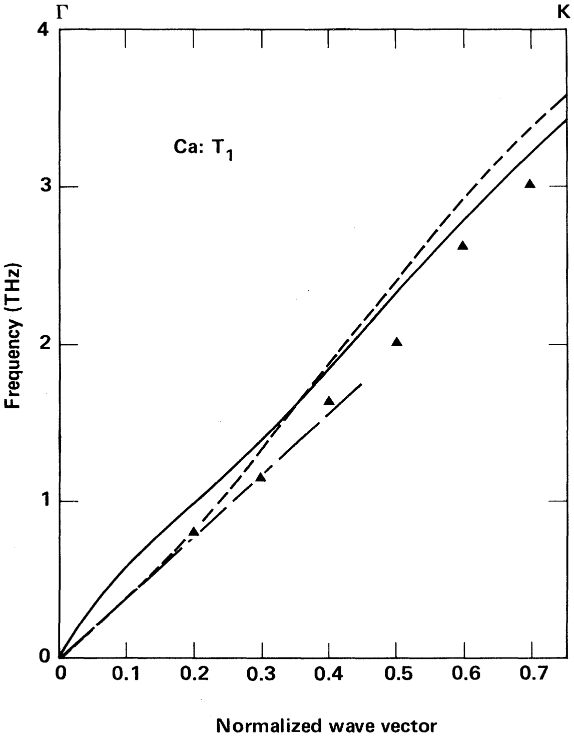

FIG. 4. Anomalous $T_1[110]$ phonon branch of Ca calculated with (solid line) and without (short dashed line) d-state hybridization in the GPT and compared against the single-crystal experimental data of Ref. 11. Long dashed line gives the approximate initial slope of the latter data and is a guide to the eye only.

1% by including only up to third–nearest-neighbor interactions. This is entirely consistent with the Born–von Kármán model assumed in analyzing the polycrystalline experimental data, where up to third-neighbor interactions were retained in Ca and up to fourth-neighbor interactions in Sr. In Sr, however, unlike Ca, a nonaxially symmetric force-constant matrix was used,[14] corresponding to the presence of angular as well as central forces, but it is not clear that this is really necessary. Certainly, the agreement between theory and experiment in Figs. 1 and 2 does not single out Sr for special treatment.

We have also calculated the density dependence of the phonon spectrum in Ca over the volume range $0.52 \leq \Omega/\Omega_0 \leq 1.24$, where Ω_0 is the equilibrium atomic volume of the metal, and have thereby determined the Grüneisen parameter $\gamma_G(\Omega)$. At normal density we calculate $\gamma_G(\Omega_0) = 1.27$, which is in reasonable agreement with the known experimental range of values[22]: 1.04–1.16.

Finally, we have obtained the corresponding bcc phonon spectra for Ca and Sr, which are of central importance to the fcc → bcc phase transitions in these metals at elevated temperature.[9,18] There are now planned experiments[12,14] to measure the bcc phonons and comparison with GPT predictions should be quite informative, especially with regard to the importance of anharmonic contributions at high temperature.

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[20] In the optimized GPT, the hybridization is described in terms of a localized *d* basis state through a *d*-state energy E_d^{vol} and appropriate plane-wave–*d*-state matrix elements. The empty-*d*-band GPT uses the most localized *d* state possible in this limit, yielding always a lower bound on the calculated hybridization. The effective strength of the hybridization can be increased by using a less localized basis state in the GPT or, more simply, by just lowering E_d^{vol} by a given amount E_d^{shift}. The latter has been done in Table I.

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