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Anomalously low [100] longitudinal phonon branch in Ba: The role of the *d* hybridization

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Recent neutron scattering experiments on single crystals of bcc Ba have revealed that the longitudinal branch along the [100] direction is lower than the transverse branch. This anomalous behavior has been studied with use of the frozen-phonon method and is shown to arise from *d*-electron interactions. The electronic-structure calculations were performed using a first-principles pseudopotential method which yielded values for the crystal lattice constant, bulk modulus, and cohesive energy in good agreement with experiment.

I. INTRODUCTION

The divalent alkaline-earth metals have long been of interest because of the different crystal structures they exhibit as a function of temperature and pressure, and also because their electronic structure is relatively simple.[1-5] The prevailing picture indicates that the free-electron-like band structure, which might be expected for these metals, is modified near the Fermi level by hybridization with a broad and largely unoccupied set of *d* bands. The amount of *d* occupation increases with pressure and it has been correlated with the volume-dependent fcc- to bcc-phase transition in Ca and Sr.[5] The *d* occupation for Ba at ambient pressure is greater than for Ca or Sr so that the bcc phase of Ba is the stable $P=0$ structure.[5] Recent diamond anvil experiments on the alkaline-earth metals with pressures exceeding 40 GPa have revealed further phase transitions to more complex structures.[6]

To include the effects of temperature and obtain a complete picture of the thermophysical properties of these elements, knowledge of the lattice vibrational energies is required. Until recently, however, the difficulty in growing large single crystals had hindered the study of the lattice dynamics of these metals and only theoretical calculations of the phonon spectra had been available.[3,4,7] The situation has improved with neutron time-of-flight experiments on polycrystalline samples of Ca and Ba which have been analyzed with Born—von Kármán models to derive phonon dispersion curves.[8,9] In addition, large single crystals of fcc Ca, bcc Ba, and the high-temperature bcc phase of Sr were grown for the first time, and the phonon-dispersion curves were measured directly using inelastic neutron scattering techniques.[10-12] The phonon-dispersion curves of Ba obtained by these direct measurements revealed that the [100] longitudinal branch is lower than the transverse branch.[11] This is quite anomalous and does not occur in the measured dispersion curves of bcc Sr.[12] Also, the previous theoretical calculations for the phonon spectra of Ba had not predicted this unusual feature.[3,4,7] The calculations described in this paper were aimed at understanding the interactions responsible for this behavior. By performing calculations both with and without the *d* states, we find that the [100] longitudinal branch is lowered because of strong interactions with the electronic states having *d*-like character.

II. PROCEDURES AND RESULTS

A. Bulk properties

Before investigating the phonons along the [100] direction, the methods and programs for Ba were tested by first evaluating some of the bulk equilibrium properties. The total-energy calculations were performed within the local-density-functional formalism,[13] using the Hedin-Lundqvist form[14] for approximating the electronic exchange and correlation energy. The electronic structure was calculated using a self-consistent, first-principles pseudopotential technique which should *not* be confused with the *empirical, perturbative methods* used previously for Ba.[2-4,7] The nonlocal ionic pseudopotential was generated from relativistic first-principles atomic calculations (without spin-orbit coupling[15]) according to the norm-conserving scheme of Hamann, Schlüter, and Chiang.[16] The method has been used successfully for a wide variety of materials and the reader is referred to our previous work on transition metals for a more complete list of references.[17] For Ba the calculation of the bulk properties was carried out for both the fcc and bcc phases. The total energy of the crystal was determined at eight different volumes, and these values were used for a nonlinear least-squares fit to obtain the equation of state. The functional form of the equation of state was the universal bonding curve,[18] although the results near the equilibrium volume are not sensitive to the analytical form chosen. The curves are shown in Fig. 1. For the bcc lattice, convergence was achieved by using 112 **k** points in the $\frac{1}{48}$th irreducible section of the Brillouin zone and a plane-wave cutoff energy of 8.5 Ry. For the fcc lattice, a similar convergence (better than 0.0002 Ry on the total energy) was obtained using 60 **k** points in the irreducible zone and the same cutoff energy. The results of the calculations are given in Table I along with the experimental values of the lattice constant, bulk modulus, and cohesive energy. The

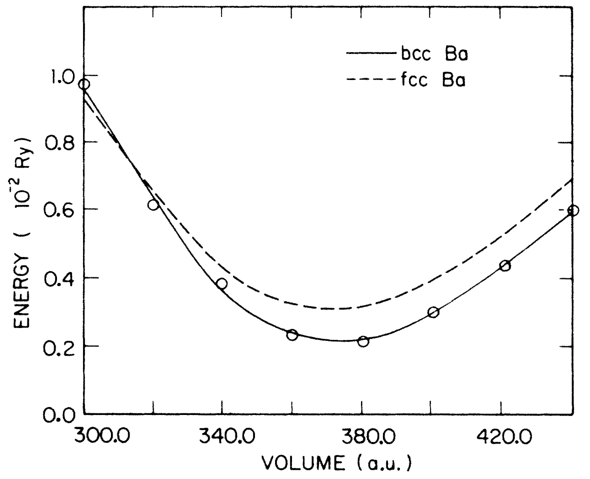

FIG. 1. Total energy (per atom) versus volume for bcc and fcc Ba. The minimum for bcc Ba corresponds to a lattice constant of 4.80 Å.

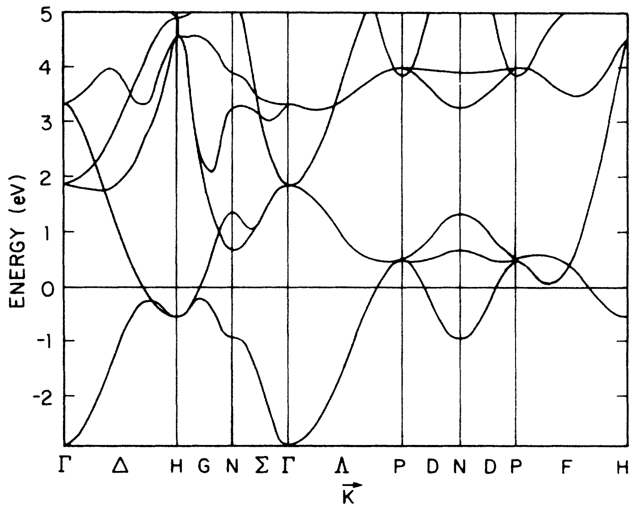

FIG. 2. Energy bands of bcc Ba calculated at the experimental volume using a first-principles pseudopotential method.

agreement between theoretical and experimental values is quite good. The 4% discrepancy with the lattice constant is larger than for more strongly bonded crystals partly because the total energy of the crystal changes very little as a function of volume as evidenced by the small bulk modulus.[19] This discrepancy is consistent with results found by other workers for Ca and Sr,[20] and might be attributed to errors due to the local-density approximation.

For comparison with previous calculations we show the energy bands along the high symmetry directions in Fig. 2. These bands were obtained using the experimental, low-temperature value of the lattice constant ($a=5.000$ Å). The corresponding electronic density of states is shown in Fig. 3. The density of states at the Fermi level, $N(E_F)$, is 1.07 states/eV atom. The experimental value of the electronic specific heat ($\gamma=2.7\pm0.5$ mJ/mol K) (Ref. 21) implies a density of states of 1.15 ± 0.2 states/eV atom which indicates a small electron-phonon enhancement. A previous non-self-consistent relativistic augmented plane wave calculation by Johansen resulted in a slightly higher $N(E_F)$ of 1.35 states/eV atom, and a band structure very similar to ours.[22] Unlike Johansen's bands we do not have any $4f$ states appearing at about 0.3 Ry above E_F, since we did not include a separate $l=3$ part to our nonlocal pseudopotential. Calculations by Duthie and Pettifor,[23] and by Herbst,[24] show that the $4f$ states remain well above E_F even at high pressures and should not affect any of the properties we deal with in this paper.

To better isolate the contribution made by the d states of Ba, we have performed calculations with the $l=2$ part of the pseudopotential shifted—which has the effect of raising the energy of the d states. The density of states for the bands with the d bands removed in this fashion is also shown in Fig. 3 and the comparison with the normal

TABLE I. Comparison of the bulk properties of Ba as calculated for the fcc and bcc structure along with the experimental values.

	Lattice constant (Å)	Bulk modulus (Mbar)	Cohesive energy (eV)
bcc Ba			
Calculation	4.80	0.11	2.01
Experiment	5.00[a]	0.105[b]	1.90[c]
fcc Ba			
Calculation	6.02	0.103	2.00

[a] W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon, New York, 1967), Vol. 2.

[b] K. Gschneidner, Jr., in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1964), Vol. 16, p. 308.

[c] L. Brewer, Lawrence Berkeley Laboratory Report No. 3720, 1977 (unpublished).

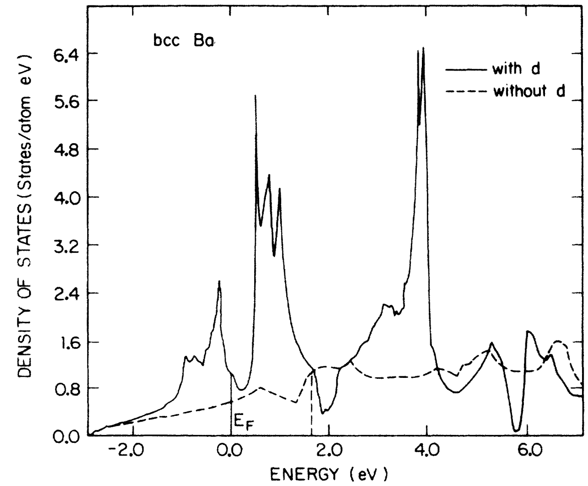

FIG. 3. Density of states for bcc Ba. The dashed curve is the result from calculations with the d bands shifted to an energy range above the scale shown. The vertical dashed line is the Fermi energy for the calculation with the d bands shifted.

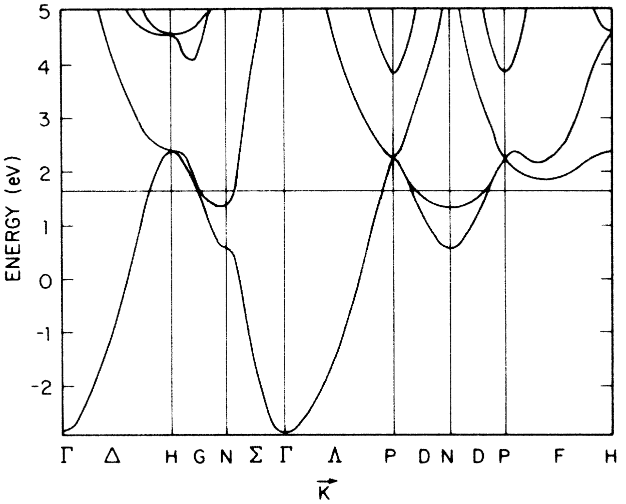

FIG. 4. Energy bands for bcc Ba with the *d* bands removed by shifting them to higher energies. The corresponding density of states is the dashed curve in Fig. 3.

density of states gives dramatic evidence for the transition-metal-like band structure of Ba. The energy bands with the *d* states shifted is shown in Fig. 4. Calculations of the total energy versus volume for Ba using this potential to shift the *d* bands well above E_F resulted in the equilibrium volume expanding by ~60% and the cohesive energy decreasing by 1.2 eV. This again emphasizes the important role played by the *d* bands in determining the physical properties of Ba.

B. Phonon anomaly

The measured phonon-dispersion curves along the [100] direction are shown in Fig. 5.[11] At reduced wave vectors larger than 0.1, where measurements could be made, the longitudinal branch is lower than the transverse, with the largest deviations (~0.3 THz) occurring in the region halfway to the zone boundary. To understand this anomalous behavior we performed frozen-phonon calculations for reduced wave vectors of 0.5 and 1.0 (the *H* point). The procedure requires the accurate calculation of the total energy of the crystal as a function of the atomic displacement. The atoms are displaced in directions corresponding to the polarization vector of the phonon being studied, and at each fixed position a fully-self-consistent band-structure calculation is performed. The total energy determined at several small values of the displacement is fit with a quadratic function, $\frac{1}{2}m\omega^2\delta^2$, from which the phonon energy $\hbar\omega$ is determined.[25] Table II lists the phonon frequencies obtained by this method. Halfway to the zone boundary the longitudinal branch is found to be lower than the transverse by ~0.2 THz in good agreement with experiment. The theoretical phonon frequencies are shown in Fig. 5 as squares. Also listed in Table II are the frequencies of the phonons halfway to the zone boundary obtained by exactly the same method, but with the $l=2$ part of the pseudopotential shifted as discussed above so that the *d* bands were no longer in the region of the Fermi level. The effect of removing the *d* bands is to raise the transverse frequency by 0.44 THz and the longitudinal frequency by 1.17 THz. Thus, without the screening from *d*-like states, the branches are ordered in the normal position and shifted to higher frequencies. This is consistent with the situation found in Sr where the *d* bands are located higher above E_F and the frequencies along the [100] direction are in the normal order.

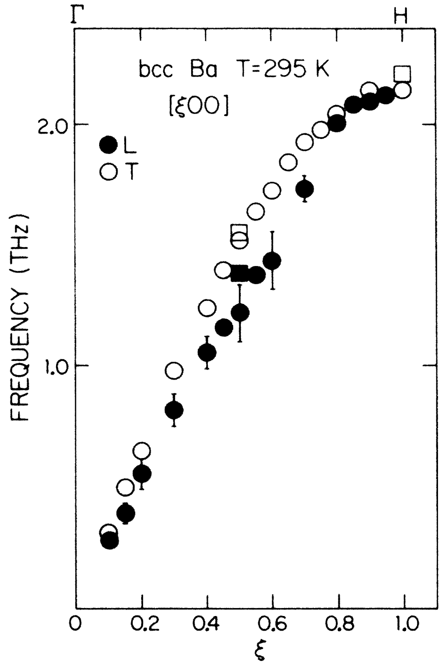

FIG. 5. The experimental phonon frequencies from Ref. 11. The corresponding theoretical phonon frequencies obtained by the frozen-phonon method are shown as squares.

TABLE II. A comparison of the experimental and theoretical phonon frequencies of bcc Ba at $\mathbf{q}=(0,0,\frac{1}{2})$ and the *H* point. The calculations were made using the experimental lattice constant.

	$\mathbf{q}=(0,0,\frac{1}{2})$ L phonon (THz)	$\mathbf{q}=(0,0,\frac{1}{2})$ T phonon (THz)	$\mathbf{q}=(0,0,1)$ *H*-point phonon (THz)
Calculation	1.38	1.55	2.20
Calculation with *d* bands removed	2.55	1.99	
Experiment[a]	1.22±0.12	1.52±0.04	2.15±0.07

[a] Reference 11.

III. CONCLUSIONS

Although there has been growing evidence that the *d* bands play an important role in determining the structure and physical properties of Ba, it is not generally appreciated how much of a "transition metal" Ba actually is. The comparison of the density of states of Ba and of a hypothetical Ba with *d* bands removed (Fig. 3) gives a clear picture of the amount of *d*-like character extending well below the Fermi level. We have shown by using the frozen-phonon method that the *d* states are responsible for the anomalously low [100] longitudinal phonon branch in Ba. The previous difficulty in finding this phonon anomaly by other methods is probably a result of the limited applicability of those methods when extended to transition metals.

ACKNOWLEDGMENTS

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