Anomalous lattice dynamics of fcc lanthanum

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First-principles pseudopotential band-structure calculations were performed for fcc La and revealed a small but sharp nesting feature of the Fermi surface. In order to investigate the relationship between this nesting and possible phonon anomalies, the phonon-dispersion curves were calculated. Along the $[\xi\xi\xi]$ direction a sharp dip in the transverse branch was found at $\xi=0.42$ in agreement with recent low-temperature neutron scattering experiments. Calculations at 14% smaller volume (corresponding to a pressure of 50 kbar) indicate that the frequencies of the phonons along the transverse $[\xi\xi\xi]$ branch decrease with pressure because of the increased magnitude of the electron-phonon matrix elements. This result helps to explain the unusual negative thermal expansion, the dramatic increase of the superconducting transition temperature, and the observed structural transition near 50 kbar.

INTRODUCTION

The unusual physical properties of La have drawn considerable attention. Compared with the isoelectronic elements Y and Sc, which are not superconducting under ambient pressure, La has a high superconducting transition temperature T_c of 6.05 K and a comparatively low Debye temperature. The rapid rise of T_c with pressure for La is the most dramatic among all the elements.[1] These properties may be associated with low-lying phonon modes and have led to speculations about the possible role of unoccupied but low-lying $4f$ electronic levels.[1,2] Understanding the properties of La in relation to the electronic structure is also important, since as the first member of the rare-earth series of elements the properties of lathanum and its compounds are frequently compared with those of other rare earths to help interpret properties associated with the occupied $4f$ levels.

Recently, a large single crystal of metastable fcc La was grown for the first time[3] and neutron scattering experiments were successfully performed at 10 K.[4] The most striking result of the measured phonon-dispersion curves is a sharp and strongly-temperature-dependent dip in the transverse $[\xi\xi\xi]$ branch near $\xi=0.42$ (Fig. 1). In this paper we present an electronic-structure calculation for fcc La and demonstrate the electronic origin of this anomaly. Additional calculations were made at 14% smaller volume, showing that the phonon frequencies of the transverse $[\xi\xi\xi]$ branch decrease with pressure. This prediction helps to explain both the unusual negative thermal expansion of fcc La at low temperature[5] and the phase transition near 50 kbar.[6]

In the last few years there have been several calculations of the electronic structure of fcc La.[7] The most extensive work (below 200 kbar) was reported by Pickett, Freeman, and Koelling,[8] who used a highly precise first-principles, self-consistent linear augmented-plane-wave (LAPW) band-structure method. Their results showed that the increase of T_c below 50 kbar is a result of increased p-d rather than d-f interactions. These authors found that the $4f$ bands, about 1 eV wide and lying ~ 2.5

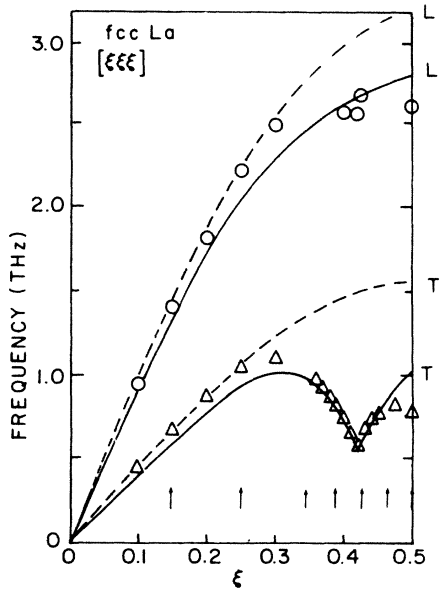

FIG. 1. Phonon-dispersion curves along the $[\xi\xi\xi]$ direction. The triangles and circles are experimental data from Ref. 4. The solid lines are the theoretical results including the D_2 contribution as explained in the text. The dashed lines are the dispersion curves from a two nearest-neighbor force-constant model used to represent the short-range interactions. The arrows show the wave vectors for which theoretical calculations were made.

eV above the Fermi level, have an average electronic occupation of ~ 0.05 for pressures up to 50 kbar. Thus the $4f$ bands play little direct role in the superconducting and other properties of fcc La for pressures below 50 kbar. Pickett *et al.* also calculated the generalized electronic susceptibility $\chi(\mathbf{q})$ (Fig. 9 in Ref. 8). As is well known, the function $\chi(\mathbf{q})$ frequently displays peaks near those wave vectors associated with phonon anomalies or structural transitions. Although the $\chi(\mathbf{q})$ calculated by Pickett *et al.*[8] increases as a function of ξ along the $[\xi\xi\xi]$ direction, indicating a strong electronic screening effect for the whole branch, it does not show any striking feature near $\xi=0.42$. Also, with increased pressure the magnitude of their $\chi(\mathbf{q})$ along $[\xi\xi\xi]$ decreases, which usually suggests less screening and hence, an increase of phonon frequencies with pressure. Since these and other calculations did not anticipate the dip observed in recent experiments,[4] we were motivated to undertake the calculations presented in this paper.

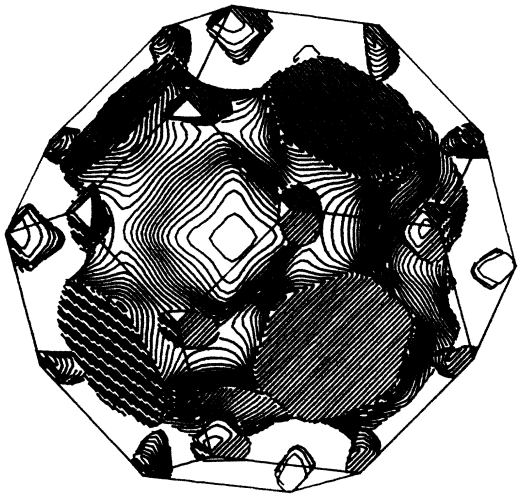

FIG. 2. Fermi surface of fcc La.

CALCULATIONS AND RESULTS

Frozen-phonon calculations[9] at a few wave vectors were first performed for the high-temperature bcc phase of La for which the phonon-dispersion curves were recently reported.[10] The calculated phonon frequencies (obtained totally from first principles) were in good agreement with experiment. Similar calculations were performed for fcc La and also agreed with experiment[4] (for the L-point transverse phonon $\nu_{\text{expt}}=0.78\pm0.03$ THz, while $\nu_{\text{theor}}=0.8$ THz, and for the longitudinal phonon $\nu_{\text{expt}}=2.61\pm0.05$ THz, while $\nu_{\text{theor}}=2.4$ THz). These calculations differ from previous ones for fcc La (Refs. 7 and 8) by excluding the $4f$ states. The motivation for removing the $4f$ levels came from speculation about the $4f$ states being responsible for the relatively low phonon frequencies in La.[1,2] If these speculations were correct, then calculations without the $4f$ states would yield values of the phonon frequencies much higher than reported experimentally. The calculations used a mixed-basis pseudopotential method[11] in which the $4f$ states were removed from the vicinity of the Fermi level by adding a repulsive term to the $l=3$ part of the angular-momentum-dependent potential. The nonlocal ionic pseudopotential was determined following the norm-conserving scheme[12] to reproduce the results of relativistic all-electron atomic calculations with spin-orbit coupling neglected.[13] The Hedin-Lundqvist[14] form of the local exchange-correlation potential was used. These are the same procedures which were successfully applied to the calculation of phonon frequencies in bcc Zr, Nb, and Mo.[9] The fact that the calculations with the $4f$ levels removed yielded phonon frequencies for fcc La in agreement with the experimental values, suggests that renormalization effects involving the empty $4f$ levels are negligible. This observation prompted the further study of the fcc phase of La using the same pseudopotential for which the $4f$ states are shifted to energies far removed from the Fermi level.

The calculated energy bands of fcc La along the high symmetry lines were found to be very similar to those of Ref. 8. Near the Fermi level, however, with the $4f$ levels missing, there is less compression of the bands near E_F, and this results in some changes in the Fermi surface (Fig. 2) and the density of states at the Fermi level. Most significantly, a small nesting feature develops in band 2 (the band which crosses the Fermi level) along the $[\xi\xi\xi]$ direction at $\xi=0.42$. The calculated $\chi(\mathbf{q})$, shown in Fig. 3, increases by $\sim 35\%$ from Γ to L, similar to the $\chi(\mathbf{q})$ of Pickett *et al.*,[8] but in addition has a small, sharp peak at $\xi=0.42$. Peaks in $\chi(\mathbf{q})$ are frequently associated with anomalies in phonon-dispersion curves. However, the calculated peak is rather small for such a large dip in phonon-dispersion curves to be anticipated. The appearance of the anomaly only in the transverse branch is also unusual. To better understand the anomaly, a detailed calculation relating the electronic response to the phonon-dispersion curves was undertaken. Such a calculation requires the evaluation of the electron-phonon matrix elements. For this task we adopted the tight-binding

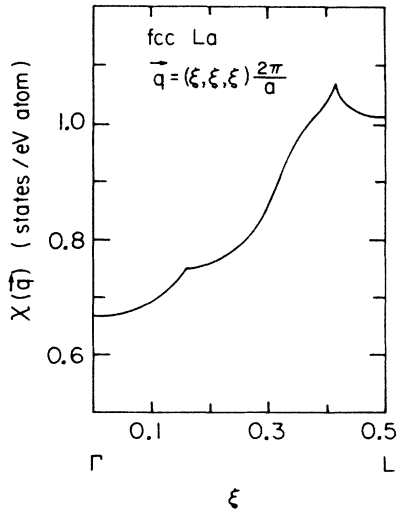

FIG. 3. Generalized susceptibility along the $[\xi\xi\xi]$ direction for fcc La.

scheme of Varma and Weber which was very successful in explaining the phonon anomalies for bcc transition metals.[15]

An empirical nonorthogonal tight-binding fit (with rms error <0.02 eV) was made to the electronic structure obtained from the first-principles pseudopotential calculation. The gradients of the hopping and overlap parameters needed for computing the electron-phonon matrix elements were determined using a similar fit to a first-principles calculation for fcc La with a 2% smaller unit-cell volume. For computing the susceptibility and matrix elements as a function of $\mathbf{q}$, the eigenvalues and wave functions from the tight-binding fit were evaluated on a mesh of 770 $\mathbf{k}$ points in the $\frac{1}{48}$th irreducible section of the Brillouin zone. To increase the resolution for those $\mathbf{q}$ vectors in the region of the anomaly, the mesh was later increased to 1638 $\mathbf{k}$ points. The part of the dynamical matrix which was calculated contains the long-range part of the lattice interactions and is responsible for the phonon anomalies. This part is commonly referred to as "D_2" and is given by

$$D_2^{\alpha\beta}(\mathbf{q}) = -\sum_{\mathbf{k}} \frac{f_{\mathbf{k}}(1-f_{\mathbf{k}+\mathbf{q}})}{E(\mathbf{k}+\mathbf{q})-E(\mathbf{k})} g^{\alpha}_{\mathbf{k},\mathbf{k}+\mathbf{q}} g^{\beta}_{\mathbf{k}+\mathbf{q},\mathbf{k}} , \quad (1)$$

where the g's are the electron-phonon matrix elements and the f's give the Fermi-Dirac occupation.[15] The calculation was restricted to intraband contributions from band 2, since bands which cross the Fermi level yield the most important contributions causing strong anomalies. For the short-range part of the dynamical matrix we followed Varma and Weber[15] and included first- and second-nearest-neighbor force constants as adjustable parameters. For convenience, these five parameters were determined by least-squares fitting to the experimental data at 19 different $\mathbf{q}$ vectors, but could have been obtained by fitting to the results of frozen-phonon calculations to produce a totally first-principle result. In any case, the short-range part of the dynamical matrix contains little structure (the dashed lines in Fig. 1). The anomaly only occurs when the strong D_2 contribution is added to the short-range part of the dynamical matrix (solid lines in Fig. 1). Analysis of the results showed that the peak in $\chi(\mathbf{q})$ comes from two small nested regions (Fig. 4) of the Brillouin zone (roughly 0.8% of the total volume). An analysis of the wave functions and matrix elements from these regions helps in understanding the size of the anomaly and its appearance in the transverse branch. The analysis is most easily accomplished by considering the d-like part of the wave functions relative to a coordinate system with the z axis along the [111] direction. Then the wave functions in these regions have a strong t_{2g} character. Figure 5 is a schematic representation of the geometrical situation showing the projection of the d orbital from the nesting region near $\mathbf{k}$ pointing along the [111] direction. The lobe of this orbital extends between lobes of opposite phase from the wave function in the $\mathbf{k}+\mathbf{q}$ nesting region. A longitudinal displacement (along [111]) maintains the cancellation in the matrix elements for nearest-neighbor interactions, while a transverse displacement produces a large change in the matrix element, and hence a large electron-phonon coupling. This mechanism

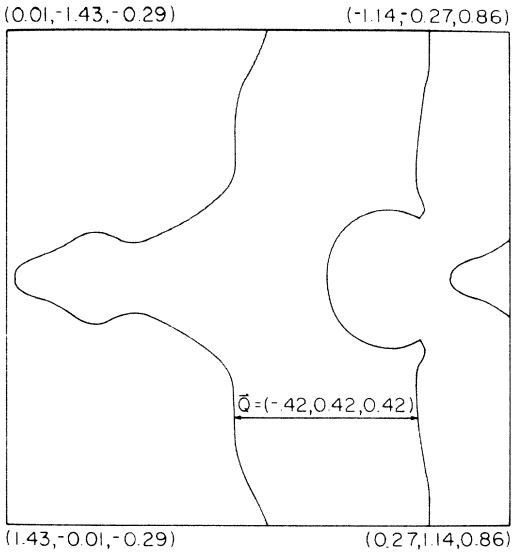

FIG. 4. An off-symmetry plane in the fcc La Brillouin zone showing the region containing the nesting feature of the Fermi surface. The coordinates are given in π/a units.

is similar to the so-called "dormant interaction" discussed by Weber.[16]

With the same tight-binding scheme we also calculated the Eliashberg function α^2F, the electron-phonon mass enhancement λ, and the superconducting transition temperature T_c. The phonon spectrum needed in the calculation was taken from a fit to the room-temperature experimental data.[4] A mesh of 140 $\mathbf{k}$ points on the Fermi surface in the $\frac{1}{48}$th irreducible section of the Brillouin zone was used. A λ value of 1.10 was found. This value together with a μ^* of 0.13 (Ref. 8) was used in the McMillan's formula as revised by Allen and Dynes[17] to obtain $T_c = 5.93$ K, a value in good agreement with experiment ($T_c^{\text{expt}} = 6.05$ K). Figure 6 is a histogram of α^2F to-

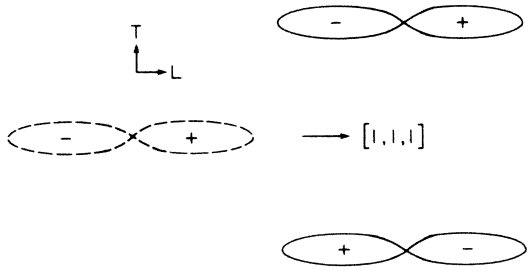

FIG. 5. Schematic diagram showing projections of d-orbital lobes for the states involved with the "dormant interaction." For [111] longitudinal motion the electron-phonon matrix elements are zero because of orbital symmetry, but for transverse motion a large coupling is obtained. The atom associated with the dashed lobe is ~ 1.1 Å above the plane of the other two atoms.

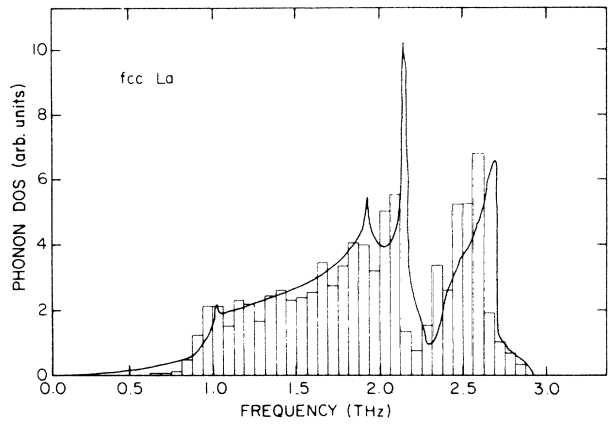

FIG. 6. The phonon density of states (DOS) (solid curve) from Ref. 4 and the calculated Eliashberg function α^2F (histogram).

gether with the phonon density-of-states curve deduced from experiment.[4] An almost constant α^2 is evident and was also deduced from tunneling and neutron scattering experiments on polycrystalline samples.[18] The position of two peaks (near 2.2 and 2.7 THz) and other general features of α^2F are comparable with the tunneling data (Fig. 6 of Ref. 18).

Finally, we repeated all the calculations for fcc La at 14% smaller volume (corresponding to ~50-kbar pressure). Similar to the results of Ref. 8, the magnitude of $\chi(\mathbf{q})$ decreased with increasing pressure. Also, the peak at $\xi=0.42$ became weaker. The D_2 contribution for the [111] transverse branch became stronger, however, because the electron-phonon matrix elements increased dramatically. This is a consequence of the strong "dormant interaction." Frozen-phonon calculations were also performed at the smaller volume to check that the short-range force constants did not increase significantly. The frozen-phonon calculations showed the transverse L-point phonon frequency decreases with pressure as expected from the larger D_2 contributions. The amount of D_2 increase was 28% near the anomaly and 21% at the L point, so we predict the dip will become stronger at higher pressure and will be the first point to go soft (at low temperature) assuming higher-order contributions to the strain energy are not large enough to force a commensurate distortion.[19] The shape of α^2F did not change much with pressure but λ increased to 1.69. Using this value of λ, $\mu^*=0.13$, and the same experimental phonon spectrum, we find $T_c=10.3$ K, again in good agreement with the experiment ($T_c^{\text{expt}}=10.0$ K).

DISCUSSION

The calculations for the phonon-dispersion curves have successfully demonstrated the origin of the recently observed[4] phonon anomaly in fcc La. In addition, reasonable values for the electron-phonon coupling parameters were obtained at normal pressure and at 50 kbar. Since we excluded the $4f$ states from the vicinity of the Fermi level in the calculations, the good agreement with experiment suggests that the almost empty $4f$ bands do not play an important role in the lattice dynamics or superconductivity of fcc La. At higher pressures we expect the influence of the $4f$ levels to become significant. Our frozen-phonon calculations at the L point for different volumes showed a softening of the low-energy transverse [$\xi\xi\xi$] branch. At low temperatures the thermal excitation of this branch dominates the contribution to the Grüneisen parameter and results in a negative thermal expansion which is highly unusual among fcc elements[5] (the negative thermal expansions of Si and Ge are of the same origin). Also, the softening of this branch with pressure is probably related to the low-temperature structural phase transition near 50 kbar.[1] Grosshans *et al.*,[6] using a diamond anvil cell, have reported superlattice reflections in fcc La beginning around 70 kbar (at room temperature) and identified the new structure as arising from the softening of the L-point phonon. Resistivity measurements[1] as a function of temperature and pressure have shown that this room-temperature transition at 70 kbar is related to the low-temperature transition near 50 kbar.[1,20] If it is indeed the L point rather than the $\xi=0.42$ phonon which goes soft at room temperature, it suggests that the nesting feature and the anomaly are reduced at higher temperature. This is supported by the neutron scattering experiments[4] which show that the dip is highly temperature dependent and at room temperature the L point is indeed the lowest frequency of the transverse [$\xi\xi\xi$] branch. It is also possible that higher-order (anharmonic) terms in the strain energy cause the lattice to lock in at the commensurate wave vector (the L point) even for lower temperatures. Pressure- and temperature-dependent neutron and x-ray experiments, along with calculations which include the $4f$ levels, are now in progress and should be able to establish quantitatively the behavior of this branch and assess the expected influence of the $4f$ electrons at higher pressures.

ACKNOWLEDGMENTS

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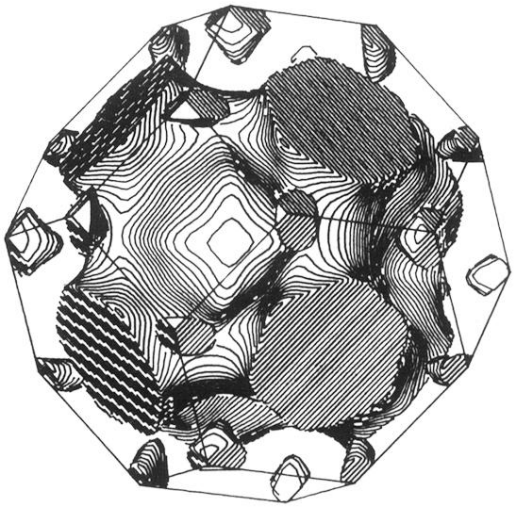

FIG. 2. Fermi surface of fcc La.