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BAND STRUCTURE AND PRESSURE-INDUCED ELECTRONIC TRANSITIONS IN CALCIUM

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The band structure of calcium has been determined at normal and reduced lattice spacings by a self-consisten APW method using a 'soft-core' approximation and Gaspar–Kohn–Sham exchange potential. It was found that calcium changes from normal metal to semimetal and back to normal metal as the lattice constant decreases, in good agreement with high-pressure experiments.

THERE HAS been considerable interest in pressure-induced electronic transitions in divalent metals.[1–6] Early treatments based upon a two-band model predicted a pressure-induced metal–semiconductor transition:[7,8] The argument went as follows: At normal pressures the s and p bands overlap yielding a metal but as the interatomic distance is decreased, the p band moves to higher energies at a faster rate than the s band and at some pressure P_c a gap appears. We have found that the energy bands of calcium cannot be described by a simple two-band model because of hybridization of the sp-band with the d-band yielding a band structure similar to that of a 3-d series metal, and that this hybridization increased with decreasing lattice constant.

Calculations of the effect of pressure on band structure and resistivity have been made by Vasvari *et al.*[2] for the alkaline earth metals using the Heine–Abarenkov model potential. For Ca they found that the Fermi surface contracted with decreasing volume until it nearly vanished at $\Omega/\Omega_0 = 0.55$ ($a = 0.74\ a_0$, where $a_0 = 10.560$ a.u. is the equilibrium lattice constant). However, the model potential used does not handle the contribution of the 3-d bands very well[9] since there are no occupied d-like core states and therefore there is less cancellation of the core potential, which greatly decreases the convergence rate of the method. At high pressures further inaccuracies are introduced by the assumption of rigid, non-overlapping atomic cores.

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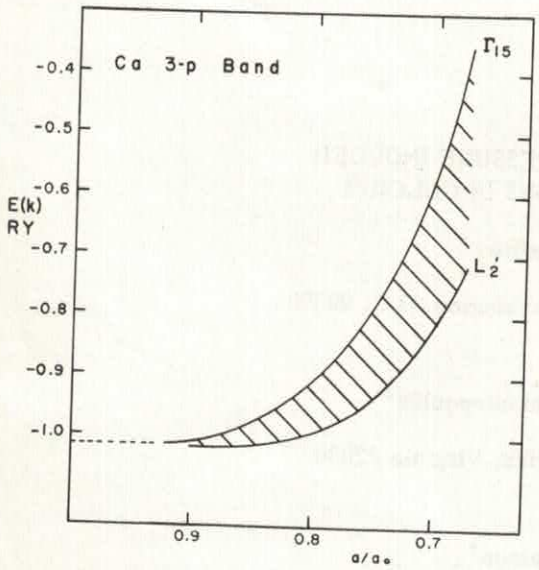

FIG. 1. Variation of the 3-p band with lattice constant. For each lattice constant the zero of energy is taken to be the corresponding muffin-tin constant.

In order to obtain a better treatment of the d-bands and the overlapping atomic cores, we have made band-structure calculations in calcium as a function of lattice spacing using a self-consistent Augmented Plane Wave (APW) method with a 'soft-core' approximation. The initial one-electron potentials were constructed by super-imposing the atomic charge densities of Herman and Skillman[10] and employing Löwdin's[11] alpha expansion. Within the 'soft-core' approximation, subsequent potentials were constructed using *both* the calculated conduction electron and the 3-p band charge densities. Figure 1 shows the pressure broadening of the self-consistent 3-p band and hence the importance of this 'soft-core' assumption.

Measurements of the soft X-ray spectra indicate an occupied conduction band width of about 0.5 Ry.[12] We have determined energy bands with two forms of the exchange potential, full Slater exchange and Gaspar–Kohn–Sham (GKS) exchange.[13] The occupied band widths at normal lattice spacing were approximately 0.15 Ry and 0.3 Ry, respectively, consequently, the GKS form of exchange was used for all subsequent calculations.

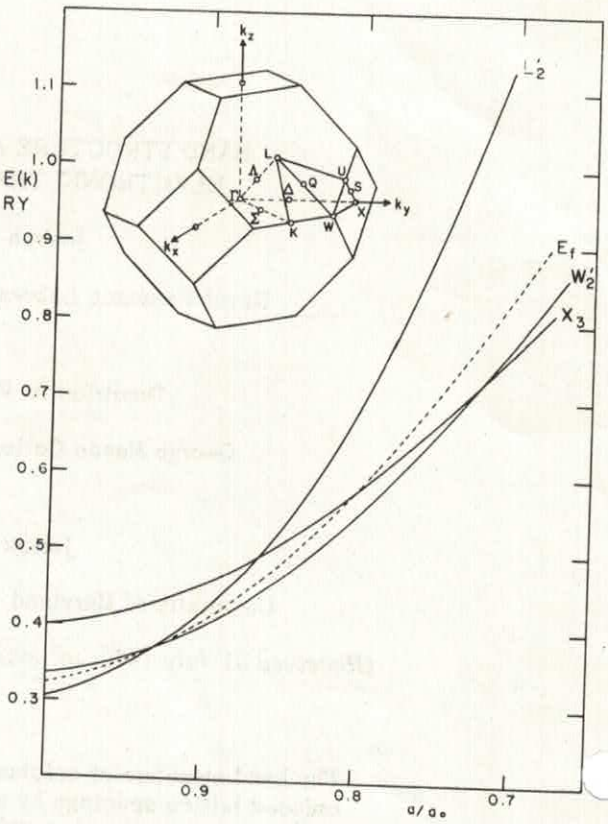

FIG. 2. Variation of the Fermi energy and the energy bands at several symmetry points with lattice constant.

At normal lattice spacing convergent results differed from the first iteration results by ~ 0.01 Ry while for $a = 0.7\, a_0$ the differences were ~ 0.07 Ry. Also at normal lattice spacing the results of this calculation differ from that of Vasvari[2] by 0.03 Ry for the s-like states, but differ by 0.34 Ry for the d-like state $\Gamma_{25'}$, confirming the poor treatment of d-electrons by the model potential.

The results of this calculation are summarized by Fig. 2 and 3. Two important crossings are seen in Fig. 2, the first at $a/a_0 = 0.93$ ($P \sim 50$ kbar) where

$$E_f = E(W_{2'}) = E(L_{2'})$$

and the second at $a/a_0 \simeq 0.8$ ($P \sim 400$ kbar) where

$$E_f = E(X_3).$$

E_f is the Fermi energy.

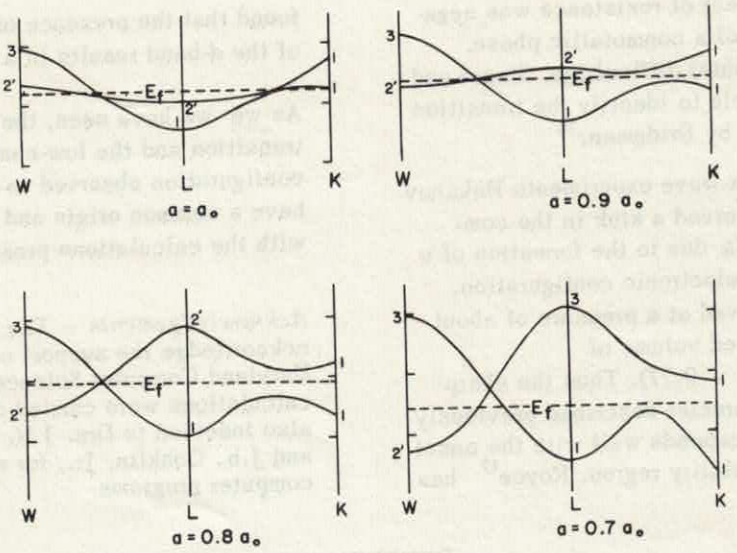

FIG. 3. Variations with lattice constant of the two lowest energy bands along the W–L–K directions.

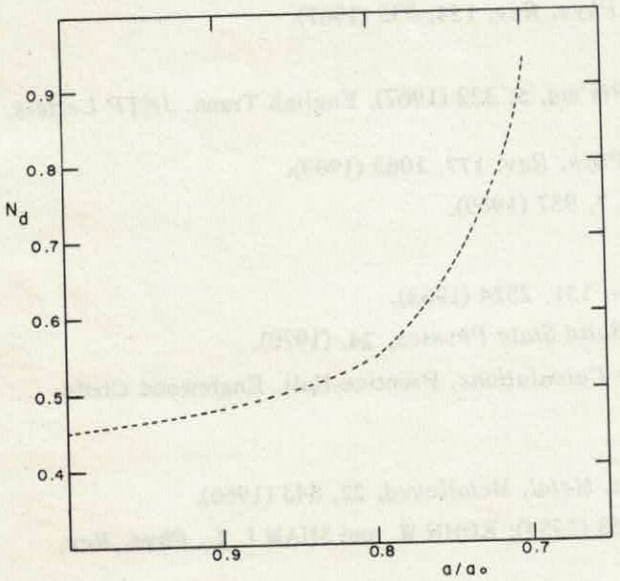

FIG. 4. Variation of the number of d-electrons with lattice constant.

The first of these crossings corresponds to a vanishing of the Fermi surface similar to that calculated by Vasvari *et al.*[2] As seen in Fig. 3 because of an accidental degeneracy along the line L–W this is not a metal–semiconductor transition, but rather a metal–semimetal transition. However, in the divalent metal ytterbium, whose band structure is similar to that of Ca, this degeneracy is removed by spin-orbit coupling[14] and pressure induced metal–semiconductor transitions have been observed.[5,6] In the K to L direction a near crossing occurs only at normal lattice spacing. Therefore over the hexagonal face of the Brillouin zone this near degeneracy is retained at normal pressures, but not at high pressures. In contradiction to these results Vasvari and Heine[15] found that the near crossing remains even at high pressure.

The second crossing in Fig. 2, $E_f = E(X_3)$ represents the d-bands falling below the Fermi energy and therefore a return to the metallic state. This corresponds to a sharp increase in the amount of d-character of the self-consistent charge density as is shown in Fig. 4. This is in good agreement with the statistical calculations of Berggren[3] who predicted a sharp increase in the number of d-electrons at about $a/a_0 = 3/4$.

Two types of experiments have yielded data on pressure-induced electronic transitions in Ca:

1. Stager and Drickamer[8] have measured the resistivity of Ca at pressures up to 600 kbar and at temperatures between 77°K and 300°K. At 77°K, for example, they observed a sluggish increase in resistance beginning at about 140 kbar followed by a sharp drop in resistance at about 390 kbar. In the high-resistance region the

temperature coefficient of resistance was negative, characteristic of a nonmetallic phase. Because of instrumental difficulties, Stager and Drickamer were unable to identify the transition at 60 kbar observed by Bridgman.[16]

2. In recent shock-wave experiments Bakanov and Dudoladov[4] observed a kink in the compression curve for Ca due to the formation of a low-compressibility electronic configuration. This kink was observed at a pressure of about 400 kbar and a reduced volume of $\Omega/\Omega_0 = 0.45$ ($a/a_0 = 0.77$). Thus the sharp increase in the d-character described previously at $a = 0.8\, a_0$ corresponds well with the onset of this low-compressibility region. Royce[17] has found that the presence of a significant population of the d-band results in a low compressibility.

As we we have seen, the semimetallic–metallic transition and the low-compressibility electronic configuration observed in these two experiments have a common origin and both are in agreement with the calculations presented here.

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Durch ein selbständiges APW–Verfahren mit Anwendung einer 'Soft-core'-Annäherung und des Austauschpotentials von Gaspar und von Kohn und Sham wurde die Bandenstruktur des Kalziums bei normalen und verkleinerten Gitterabständen bestimmt. Es wurde festgestellt, dass bei Abnehmung der Gitterkonstante das Kalzium sich von normalem Metall zum Halbmetall und wieder zum normalen Metall verändert, in guter Übereinstimmung mit Hochdruckversuchen.