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Electronic Structure of Ca, Sr, and Ba under Pressure

B. VASVARI*
Atommagkutato Intezete, Debrecen, Hungary

AND

A. O. E. ANIMALU†
W. W. Hansen Laboratories of Physics, Stanford University, Stanford, California

AND

V. HEINE‡
Department of Physics and Institute for the Study of Metals, The University of Chicago, Chicago, Illinois

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The electronic-band structure of Ca, Sr, and Ba has been calculated for the fcc phase, in the case of Ca and Sr as a function of atomic volume up to 60% compression. A few preliminary results for the bcc phase are given for comparison. The potential for the calculation was set up with the model potential of Abarenkov, Animalu, and Heine, with the nonlocal terms calculated exactly in the screening and in the matrix elements. The band structure, which is basically nearly-free-electron-like, does not have the simple form of *sp* bands near the Fermi level, but is dominated by the admixture of *d* components there. The fcc phase does not become a semiconductor at small atomic volumes, as has previously been suggested, but becomes a semimetal because of a line of degeneracy between the lowest two bands which is split only by spin-orbit coupling.

I. INTRODUCTION

THE main motivation for the present work is the change in the electrical properties of the alkaline-earth metals under pressure. In calcium,[1,2] there is a marked rise in resistivity and a negative temperature coefficient of resistivity $\partial R/\partial T$ at 300–400 kbar, i.e., at $\Omega/\Omega_0 \approx 0.5$, where Ω is the atomic volume.[3] Unfortunately, the crystal structure is not known in this state because of the various phase transitions induced by the pressure. Sr shows a negative temperature coefficient $\partial R/\partial T$ at 35 kbar in the fcc (face-centered-cubic) phase before the transition to bcc (body-centered-cubic).[1,2,4,5] Barium, already bcc at zero pressure, has positive $\partial R/\partial T$ at all[1,2] pressures P. Ca and Sr, therefore, would appear to become semiconductors or semimetals at certain pressures.

The traditionally supposed explanation has been as follows[1,6,7]: As we decrease the interatomic spacing of a set of divalent atoms from some large value, the material is at first an insulator with one full band derived from the atomic *s* states. As the distance decreases, the bands broaden and the *sp* band gap between the first and second bands decreases. At some spacing, the gap passes through zero and then increases in magnitude, with the *p* state at the gap lying below the *s* state. At that stage, increase of pressure will make the material less metallic and may actually result in a semiconductor, if the increase in band gap outstrips the increase in kinetic-energy differences around the zone faces. This

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[‡] Part of the work was supported by the National Aeronautics and Space Administration while the author was a visitor at the Institute for the Study of Metals, The University of Chicago, Chicago, Illinois. Permanent address: Cavendish Laboratory, Cambridge, England.

[1] H. G. Drickamer, Solid State Phys. **17**, 1 (1965).

[2] R. A. Stager and H. G. Drickamer, Phys. Rev. **131**, 2524 (1963).

[3] F. P. Bundy and H. M. Strong, Solid State Phys. **13**, 81 (1963), quoting data by Bridgman on p. 116.

[4] A. Jayaraman, W. Klement, and G. C. Kennedy, Phys. Rev. **132**, 1620 (1963); Phys. Rev. Letters **10**, 387 (1963).

[5] D. B. McWhan and A. Jayaraman, Appl. Phys. Letters **3**, 129 (1963).

[6] N. F. Mott, Phil. Mag. **13**, 989 (1966).

[7] N. F. Mott (private communication).

picture emerges both from a tight-binding approach,[8] and from nearly-free electrons with a normal kind of pseudopotential.

The present series of band-structure calculations for Ca, Sr, and Ba, over a wide range of atomic volumes, was undertaken in order to elucidate what happens in more detail. This cannot, of course, be done completely until the structures of the various phases have been determined experimentally. We find that the results differ in two essential respects from the above picture. It is not purely a question of s-like and p-like states, since the relevant states near the Fermi level are severely perturbed by being mixed up with the lowest part of the empty d band just above them. One consequence is that in the fcc structure, symmetry requires a line of degeneracy between the first and second bands, so that the material can become only a semimetal with a very small area of Fermi surface. This is in disagreement with the preliminary results on the band structure of Ca announced by Altmann and Cracknell.[9] In the bcc structure, the two bands are joined along a symmetry line, and the material probably remains a fairly good metal.

Two other points of interest are: Firstly, can we say anything from the band structures about the relative stability of the fcc and bcc phases to account for the phase transition between them at high pressure? Secondly, there are the incomplete de Haas–van Alphen data on Ca by Condon and Marcus,[10] and their differing interpretation[9,10] according to the band-structure calculations of Harrison[11] and of Altmann and Cracknell.[9] In the present paper, we give the results for the band structures, describe the method of calculation, and generally discuss the electronic structure of the three metals, which is of interest in itself. In future publications, we shall base on them more detailed discussion of the resistivity of Ca, Sr, and Ba under pressure,[12] the shape of the Fermi surface in Ca at atmospheric pressure,[13] and the phonon spectra[14] of Ca, Sr, and Ba calculated from the same potentials, for comparison with the relevant experimental data.

II. THE BAND-STRUCTURE CALCULATIONS

TABLE I. Parameters for the potential in atomic units.

	R_M	A_0	A_1	A_2	Ω_0	R_c
Ca	3.6	0.57	0.61	0.92	293.5	2.0
Sr	3.6	0.53	0.54	0.88	380.2	2.4
Ba	3.6	0.47	0.41	0.99	424.1	2.7

The potential was set up using the model potential of Abarenkov and Heine[15] in precisely the manner described by Animalu and Heine.[16] The parameters used are given in Table I, where the symbols have the meaning defined there.[16] Ω_0 is the atomic volume at $P=0$. Since the band structure was required as a function of atomic volume Ω, the self-consistent screening by the conduction electrons was recalculated appropriately for each value of Ω/Ω_0. We emphasize that the full nonlocal nature of the potential was used in calculating all matrix elements,[16] and in the self-consistent screening by the electron gas.[17] The higher angular-momentum components of the potential, and the orthogonality and correlation corrections, were all incorporated in the manner of Ref. 16. The A_l were evaluated at an energy corresponding to the Fermi level at $\Omega=\Omega_0$, as described in Ref. 16, and then not further varied: The error is essentially negligible as far as the band structure near the Fermi level is concerned.

In order to set up the secular equation (see below), matrix elements of the potential were generated[16] between plane waves $\mathbf{k}+\mathbf{g}_i$, $\mathbf{k}+\mathbf{G}_n$, where $\mathbf{k}$ is the wave vector in the reduced Brillouin zone. For the fcc structure $\mathbf{g}_i$ are the set of 8 reciprocal lattice vectors (000), $(\bar{1}\bar{1}1)$, $(\bar{1}\bar{1}\bar{1})$, $(\bar{2}00)$, $(0\bar{2}0)$, $(\bar{2}\bar{2}0)$, $(\bar{1}11)$, and $(\bar{1}1\bar{1})$, all in units of $2\pi/a$, which give the lowest two levels in the free-electron approximation at W in the zone. The $\mathbf{G}_i$ are all remaining 105 reciprocal lattice vectors of type {111}, {200}, {220}, {311}, {222}, {400}, {420}, and {331}. The damping factor $D(q)$ of Ref. 16 was applied to reduce spurious oscillations and termination errors from the high Fourier components, though the convergence in all respects turned out to be sufficiently rapid that the damping factor could have been, and would better have been, omitted.

The matrix elements between the $\mathbf{k}+\mathbf{g}_i$ were treated exactly in an 8×8 secular equation. The matrix elements connecting these with the $\mathbf{k}+\mathbf{G}_n$ were treated correct to second order by folding them[18] into the 8×8 secular equation, which becomes (in Ry)

$$\det|H_{ij}(\mathbf{k})-E\delta_{ij}|=0, \tag{1a}$$

$$H_{ij}=(\mathbf{k}+\mathbf{g}_i)^2\delta_{ij}+\langle\mathbf{k}+\mathbf{g}_i|V|\mathbf{k}+\mathbf{g}_j\rangle+\Sigma_{ij}, \tag{1b}$$

$$\Sigma_{ij}=\sum_n \frac{\langle\mathbf{k}+\mathbf{g}_i|V|\mathbf{k}+\mathbf{G}_n\rangle\langle\mathbf{k}+\mathbf{G}_n|V|\mathbf{k}+\mathbf{g}_j\rangle}{E-(\mathbf{k}+\mathbf{G}_n)^2}. \tag{2}$$

Note that the summation excludes the basic eight $\mathbf{g}_i$ which are completely taken account of in the secular equation itself. The E in the energy denominator should strictly be the E being calculated[19] as in the Brillouin-Wigner perturbation theory, and was set equal to k^2 with essentially negligible error near the Fermi level. The sum was evaluated at a point $\mathbf{k}_0=k_F5^{-1/2}$ (2,1,0)

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[8] N. F. Mott and H. Jones, *Theory of the Properties of Metals and Alloys* (Clarendon Press, Oxford, England, 1936), p. 74.

[9] S. L. Altmann and A. P. Cracknell, Proc. Phys. Soc. (London) **84**, 761 (1964).

[10] J. H. Condon and J. A. Marcus, Phys. Rev. **134**, 446 (1964).

[11] W. A. Harrison, Phys. Rev. **131**, 2433 (1963).

[12] B. Vasvari and V. Heine, Phil. Mag. (to be published).

[13] B. Vasvari (to be published).

[14] A. O. E. Animalu (to be published).

[15] I. Abarenkov and V. Heine, Phil. Mag. **12**, 529 (1965).

[16] A. O. E. Animalu and V. Heine, Phil. Mag. **12**, 1249 (1965).

[17] A. O. E. Animalu, Phil. Mag. **11**, 379 (1965).

[18] See, for example, P. W. Anderson, *Concepts in Solids* (W. A. Benjamin, Inc., New York, 1963), p. 37; also Refs. 17 and 19.

[19] M. H. L. Pryce, Proc. Phys. Soc. (London) **63**, 25 (1950).

on the free-electron Fermi sphere (radius k_F) near W, and a similar point near L. All the contributions Σ_{ij} differed by no more than 0.007 Ry between the two points, and most by much less. Since the nonlocal screening part of each matrix element involves a two-dimensional integral, the Σ_{ij} were set equal to their value at $\mathbf{k}_0$ for exploring the band structure over a region of $\mathbf{k}$ space where $\mathbf{k}_0$ was taken as representative of points near the Fermi level E_F in 1/48th part of the zone. Inspection of our matrix elements shows in retrospect that it would have been even better to recalculate it at each point, but with the local screening approximation[17] in the matrix elements in the numerator: The difference between local and nonlocal screening is quite small[17] at such large values of $|\mathbf{G}-\mathbf{g}|$, and with nonlocal screening it could have been done without an excessive use of computing time. The Σ_{ij} were about 0.01 Ry or less, from which we can conclude that third-order terms omitted beyond the basic set of eight $\mathbf{g}$'s are negligible. As regards the diagonal matrix elements of the potential V, all electrostatic effects, including screening, contribute a constant V_{000} which can be dropped from the secular equation. The correct diagonal matrix element of the nonlocal part of the potential can be calculated in the same way as in all the other matrix elements. It is a function of $|\mathbf{k}+\mathbf{g}|$ only, varying negligibly around the Fermi surface, and was ignored. We believe this is the first band-structure calculation based on the model potential which takes into account, in detail, its nonlocal nature, and we have therefore also described the further small improvements which our experience suggested, and which would have been made in the calculations had not all three authors left Cambridge at that time. However, in view of the smallness of these improvements and the care in setting up the potential,[15–17] we believe the total physical reliability of the results (*including* uncertainties in the potential) is as good as many published band-structure calculations.

The results for $E(\mathbf{k})$ are shown in Figs. 1–6. The labeling follows the standard notation.[20] E_{F0} is the free-electron Fermi level. In Fig. 2 for Ca we show only the bands near E_F as a function of atomic volume Ω, since only they are relevant to the electrical properties; the bottom of the band at Γ is always at $E=0$, apart from some small corrections from Σ_{ij}, as seen in Figs. 1, 3, and 4. The largest compression for $\Omega/\Omega_0=0.4$ corresponds[3] to more than 400 kbar (probably 500–600 kbar).[3] The variation of $E(\mathbf{k})$ with volume for Sr and Ba is similar, as shown by the variation of the symmetry points in Fig. 5. We give only $\Omega=\Omega_0$ for Ba for comparison with Ca and Sr, since in reality the structure is bcc. The bands in Figs. 1, 3, and 4 were calculated at closely spaced points along symmetry lines (e.g., 15 along WX and WL). In Fig. 6 we give some preliminary results for Ca in the bcc structure.

It is worthwhile remarking that the potential is considerably more nonlocal in the present case than is usually found among simple metals. If we compare matrix elements $\langle\mathbf{k}|V|\mathbf{k}'\rangle$ with $k\approx k'\approx k_F$ for forward

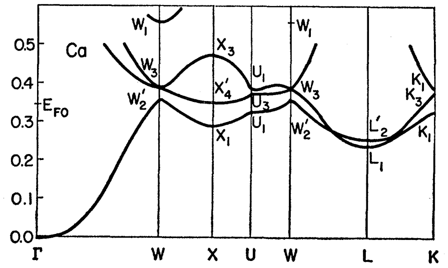

FIG. 1. Band structure of Ca in fcc phase at $\Omega/\Omega_0=1.0$. E_{F0} is the Fermi level for a *free*-electron gas.

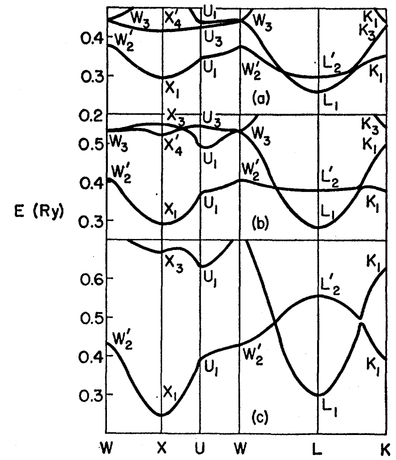

FIG. 2. Band structure of Ca in fcc phase at Ω/Ω_0 equal to (a) 0.8, (b) 0.6, (c) 0.4.

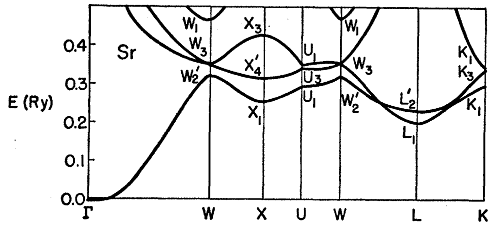

FIG. 3. Band structure of Sr in fcc phase at $\Omega/\Omega_0=0.9$.

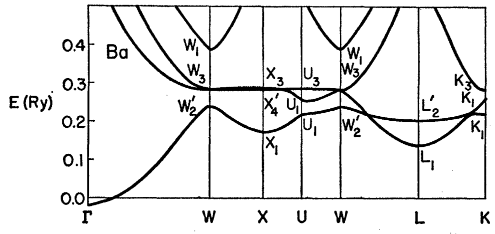

FIG. 4. Band structure of Ba in fcc phase at $\Omega/\Omega_0=1.0$.

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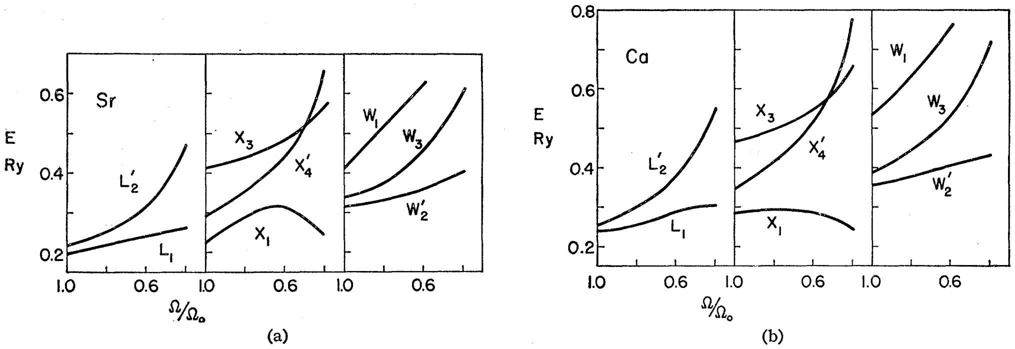
[20] L. P. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. **50**, 58 (1936).



(a) (b)

FIG. 5. Variation of $E(\mathbf{k})$ at symmetry points as a function of Ω/Ω_0 for (a) Ca, and (b) Sr in fcc phase.

scattering (**k** and **k**′ parallel), and backward scattering ($\mathbf{k}\approx-\mathbf{k}'$), but the same $|\mathbf{k}-\mathbf{k}'|$, we find the differences for aluminum just as large as for calcium, in both cases about[21] 0.1 E_{F0}. But what we are really interested in is scattering more or less across the Fermi sphere from symmetry points. In Al, the lowest levels at L, X, and W can be described by $V(111)$ and $V(200)$ matrix elements which are approximately the same for the three points.[11] However, in Ca (Fig. 1), the fact that the s-like levels, L_1 and X_1, lie below the p-like ones, L_2' and X_4', implies negative values for V(111), and $V(200)$, respectively (Table II), which in turn would give W_1 lying below W_2' and W_3 at the zone corner. However, W_1 is found to lie highest by quite a margin. The same is found even more strongly in Sr and Ba (Figs. 3 and 4). It is clear that a scheme with constant $V(111)$ and $V(200)$, used so successfully for Al,[22] cannot remotely work for the alkaline earths. We believe the reason for the particular nonlocality observed here lies in the larger difference between A_2 and A_0, A_1 in the model potential (compare Table I of the present paper and Ref. 16), which increases the nonlocal term in the potential.[23] The unusual shape of the pseudopotential form factors[16] $v(q)$, which is also shown by[16,24] K, Rb, and Cs appears related to the same difference.

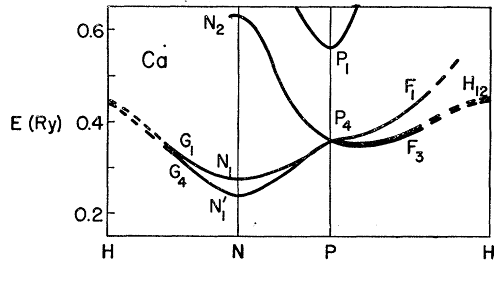


FIG. 6. Band structure of Ca in bcc phase. The results for the lowest bands near H are uncertain by something of the order of 0.05 Ry (Ref. 28).

III. DISCUSSION

We have already noted that the bands are basically nearly-free-electron-like. However, no scheme with *constant* (111) and (200) pseudopotential matrix elements, which has been a remarkably successful approximation[22] for sp bands, can describe the bands of the alkaline earth metals near the Fermi level E_F. Here the $l=2$ component of the potential is abnormally attractive compared with Mg, Zn, Cd, Hg, and elements to the right of them in the periodic table.[16] In other words, the states near E_F already have a considerable d component. This was already noted by Manning and Krutter,[25] and is hardly surprising, since, in the Ba atom, for example, the $6s\ 5d$ configuration lies[26] below $6s\ 6p$ by about $\frac{1}{2}$ eV. We can see this explicitly in the band structures. The order of levels at W and K, the low energy of X_1 and L_1, the depression of X_3 from its free-electron value, are all characteristic of d bands (compare, for example, the bands calculated by Wood[27] for Fe); and the same applies at P and H for the bcc structure. The effect increases with pressure (Fig. 5); the bonding p states L_2' and X_4' increase in energy relative to the antibonding s states L_1 and X_1 because the latter are depressed by the hybridization with the empty d band above. The simple picture of Sec. I, with the p level decreasing in energy with respect to the s level, simply does not apply. We also note (see, for example, the levels at X in Figs. 1, 3, and 4) that the admixture of d component increases somewhat from

TABLE II. Effective pseudopotential parameters $V_{\text{eff}}(111)$ and $V_{\text{eff}}(200)$ obtained by fitting a nearly-free-electron model to the lowest set of levels at symmetry points in the band structure of Ca at $\Omega/\Omega_0=1$.

	L	X	W	K
$V_{\text{eff}}(111)$	−0.007	···	0.048	0.021
$V_{\text{eff}}(200)$	···	−0.044	0.021	−0.023

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[21] A. O. E. Animalu (unpublished).

[22] W. A. Harrison, Phys. Rev. **118**, 1182 (1960); N. W. Ashcroft, Phil. Mag. **8**, 2055 (1963).

[23] V. Heine and I. Abarenkov, Phil. Mag. **9**, 451 (1964).

[24] N. W. Ashcroft, Phys. Rev. **140**, 935 (1965).

[25] M. F. Manning and H. M. Krutter, Phys. Rev. **51**, 761 (1937).

[26] C. Moore, in *Atomic Energy Levels*, Natl. Bur. Std. (U.S.) Circ. No. 467 (U. S. Government Publishing and Printing Office, Washington, D. C., 1949), Vol. 3, p. 131.

[27] J. H. Wood, Phys. Rev. **126**, 517 (1962).

Ca to Sr, and markedly in Ba, as one would expect from the atomic levels.[26]

We see from Fig. 1 that there will be pockets of electrons around L. The hole surface consists of either pockets of holes at W or a connected "monster" as suggested by Harrison,[11] in either case in disagreement with Altmann and Cracknell.[9] Detailed calculations of E_F and the shape of the Fermi surface for comparison with experiment[10] are in progress.[13]

As regards the electrical properties, we have already noted that the simple *sp* picture (Sec. I) does not apply. Figs. 2, 3, and 5(b) show the Fermi surface of Ca and Sr must decrease with pressure, until at $\Omega/\Omega_0=0.6$ it has practically disappeared. It cannot disappear completely and give a semiconductor, as suspected by Altmann and Cracknell,[9] because of the degeneracy between the first two bands along LW [Fig. 2(c)]. However, the band overlap appears to be of the order of 0.01 Ry or less, which could result in a negative $\partial R/\partial T$ at room temperature. The relevance of this to the observations on Ca is not clear, since the structure at $P=300$–600 kbar is uncertain. More detailed calculations and discussion of the resistivity of Ca, Sr, and Ba will be reported elsewhere.[12] The band structure of Sr changes with pressure similarly to that of Ca (Fig. 5), and a negative $\partial R/\partial T$ would be expected in the fcc phase at $\Omega/\Omega_0\approx0.55$. Experimentally, it is observed in this phase[4] at 30 kbar[1,2] ($\Omega/\Omega_0=0.8$, Ref. 3), so that agreement is not quantitative.

For the bcc structure, we observe (Fig. 6) that the first two bands are degenerate along all zone edges PH. As we go from Ca to Ba, or decrease Ω/Ω_0, the gap at N opens up[28] and H_{12}, which is pure d symmetry, drops in energy relative to P_4. We therefore expect this structure to be a metal at all pressures, though the Fermi surface would be very small when H_{12} is at the same energy as P_4.

A few tentative comments may perhaps be offered about the relative stability of the fcc and bcc phases. The energy differences are so small that speculation is dangerous, but the following aspects do appear to indicate at least a consistent picture. Calculations of the phonon spectra with the same potentials as in Sec. II, indicate somewhat higher phonon frequencies for the fcc phase, enhancing the relative stability of the bcc phase at high temperature, as observed[4] for Ca and Sr. As regards the total energy at zero temperature, the $E(\mathbf{k})$ in the major parabolic part of the first band is independent of structure, so that energy differences between phases are due to the states near the Fermi level. We have seen that these states are dominated by the admixing of d components, so that the alkaline earths behave somewhat like the early transition metals, i.e., tend to be bcc. Ba, where the d effect is strongest, is already bcc at $P=0$, and Sr becomes so[5] at 35 kbar when, as we have seen, the d effect increases with reducing Ω/Ω_0. The structures of the high-pressure phases of Ca do not appear to be well established.[4] In tight-binding terms, the preference for bcc early in the transition series has been attributed to a high density of states at the bottom of the d band for bcc, whereas the fcc structure gives an asymmetrical d band with a longer tail of low density at low energy.[29] In our $E(\mathbf{k})$ this is seen in the triple degeneracy of P_4 and the double degeneracy along PH in the bcc case, whereas all the lowest d like states are nondegenerate for fcc. From Fig. 6 we estimate E_F for the bcc phase of Ca at 0.36 Ry, compared with 0.325 Ry for the fcc structure as mentioned above,[30] which means fcc is definitely favored. For Ba, the analogous figures are 0.240 Ry (bcc, Ref. 25), and 0.225 Ry (fcc, Fig. 4), which would still favor fcc, but the difference is much smaller and the trend is in the right direction.

ACKNOWLEDGMENTS

It is a pleasure to record the helpful and stimulating discussion with Professor N. W. Ashcroft and Professor W. A. Harrison, and with Sir Nevill Mott, as well as the help of the Mathematical Laboratory staff, Cambridge, where the calculations were carried out.

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[28] B. Vasvari and A. E. O. Animalu (unpublished). $E(\mathbf{k})$ was calculated for bcc Ca, Sr, and Ba for $\Omega/\Omega_0=1.0$ to 0.4. The results suffer from some uncertainty near H which could not be eliminated before departure from Cambridge, so that we only describe the systematic variations found.

[29] J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

[30] The absolute error in these rough estimates could easily be ±0.01 Ry, but comparison of the energies calculated at symmetry points for fcc and bcc Ca and Ba leaves the stated trend in no doubt.