Energy Band and Fermi Surface of Divalent Metals under Pressure

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The energy band structure of face-centered cubic metals Ca, Sr, and Ba was investigated by a pseudopotential-like approximation, using the screened model potential of Abarenkov, Heine, and Animalu. All three of the metals exhibit a negative energy gap at atomospheric pressure, the magnitude of which tends to zero with increasing pressure. According to a symmetry demanded degeneracy along the line WL of the Brillouin zone, the transition to semiconductors with positive energy gap seems to be unlikely. The Fermi surface consists of holes in the first zone around the points W and electrons in the second zone around the points L. The dimensions of these surfaces are also decreasing under pressure. The Fermi surface of Ca was studied in detail. Numerical results for the de Haas–van Alphen periods cyclotron masses, are given. The pressure dependence of electrical resistivity of Ca was calculated and found to be in qualitative agreement with the experiments.

I. INTRODUCTION

This is a paper reporting calculations about the band structure, Fermi surface, and some related phenomena of the face-centered (fcc) cubic divalent metals Ca, Sr, and Ba. The method used was a pseudopotential-like approximation with a screened model potential developed by Abarenkov, Heine, and Animalu.[1] Using this potential, the band structure of fcc Ca, Sr, and Ba under pressure has already been published under common authorship with Animalu and Heine in the last year.[2] Later, a simple model for the electronic conductivity was developed in order to give at least a qualitative explanation of the pressure dependence of electrical resistivity of Ca.[3] After a brief summary of the method and the earlier results, I should like to show here some pictures about the Fermi surface of metal Ca which serves as a very good representative for the other two metals as well.

II. THE SCREENED MODEL POTENTIAL

The concept of the screened model potential uses a simple semiempirical potential of the free ion. This potential is an energy- and angular-momentum-dependent one and may be written as follows:

$$V_M(\mathbf{r})=\sum_l V_l(E,\mathbf{r})P_l. \tag{1}$$

Here the operators P_l project any function into the lth subspace of the angular momentum operators and

$$\begin{aligned} V_l(E,\mathbf{r}) &= -A_l(E) \qquad \text{for } r<R_M \\ &= -Z/r \qquad \text{for } r\geq R_M. \end{aligned} \tag{2}$$

The restrictions on the parameters $A_l(E)$ were that the model potential V_M should give as energy eigenvalues the experimentally measured energies of the free atom. From this requirement the parameters $A_l(E)$ can be determined and they proved to be rather smooth functions of the energy E. Then they were interpolated or extrapolated to the metal energies.

Calculating the screening of the bare ionic potentials one starts from the Hartree–Fock equation of the free electron gas

$$H_{\mathrm{HF}}\psi_{\mathbf{k}}=E(\mathbf{k})\psi_{\mathbf{k}}, \tag{3}$$

where the functions $\psi_{\mathbf{k}}$ are simple plane waves and H_{HF} is the free electron Hartree–Fock Hamiltonian. Inserting the metal ions into this electron "jellium," one can suppose that

$$\psi_{\mathbf{k}}\rightarrow\psi_{\mathbf{k}}+\delta\psi_{\mathbf{k}}\equiv\phi_{\mathbf{k}} \tag{4}$$

and the new $\phi_{\mathbf{k}}$ satisfy the wave equation

$$(H_{\mathrm{HF}}+V_{\mathrm{ion}}{}^{\mathrm{bare}})\phi_{\mathbf{k}}=\epsilon(\mathbf{k})\phi_{\mathbf{k}}. \tag{5}$$

This equation can be transformed into the form

$$(H_{\mathrm{HF}}+U)\psi_{\mathbf{k}}=\epsilon(\mathbf{k})\psi_{\mathbf{k}}, \tag{6}$$

where the new potential U contains the variation $\delta\psi_{\mathbf{k}}$, too, besides $V_{\mathrm{ion}}{}^{\mathrm{bare}}$. If one supposes that the corrections $\delta\psi_{\mathbf{k}}$ have to be determined self-consistently by the potential U itself, then in the terms of the first-order perturbation formalism one can derive a Dyson-type equation for the U, the first-order solution of which can be written as

$$\langle\psi_{\mathbf{k}}\mid U\mid\psi_{\mathbf{k}}\rangle=\frac{V_{\mathrm{ion}}{}^{\mathrm{bare}}(q)}{\epsilon(q)}+F(\mathbf{k}',\mathbf{k})+I(q), \tag{7}$$

where $q=\mid\mathbf{k}'-\mathbf{k}\mid$, and

$$\epsilon(q)=1-\frac{4\pi e^2}{\Omega q^2}[1-f(g)]\sum_{\mathbf{l},\mathbf{n}}\frac{n(\mathbf{l})-n(\mathbf{m})}{\epsilon(\mathbf{l})-\epsilon(\mathbf{m})}. \tag{8}$$

The $F(\mathbf{k}',\mathbf{k})$ is the nonlocal part of the original bare ion potential and $I(q)$ is a relatively small correction depending on F. Anybody interested in the details should consult the original papers.[1] From these matrix

[1] I. Abarenkov and V. Heine, Phil. Mag. **12**, 529 (1965); V. Heine and I. Abarenkov, *ibid.* **9**, 451 (1964); A. O. E. Animalu and V. Heine, *ibid.* **12**, 1249 (1965); and A. O. E. Animalu, *ibid.* **11**, 379 (1965).
[2] B. Vasvári, A. O. E. Animalu, and V. Heine, Phys. Rev. **154**, 535 (1967).
[3] B. Vasvári and V. Heine, Phil Mag. **15**, 731 (1967).

elements an 8×8 secular equation was built up. With Brillouin–Wigner-type perturbation theory, further sets of matrix elements were folded into our 8×8 energy matrix giving our basic equation

$$\det | H_{ij}(\mathbf{k}) - \epsilon(\mathbf{k}) \delta_{ij} | = 0. \qquad (9)$$

We have to emphasize the nonlocality of our screened model potential which is coming from the **k**-dependent term $F(\mathbf{k}, \mathbf{k}')$. In this respect our approximation differs radically from the simple pseudopotential approach proposed by Harrison which applies only to a few **k**-independent matrix elements in order to fit the experimentally determined Fermi surface of polyvalent metals. The nonlocality is a rather strong effect in the case of our three metals, which is, I believe, the manifestation of the increasing role of the d bands.

It is also important to note that the full nonlocality (full **k** dependence) had been taken into account in the explicit expression of the energy matrix $H_{ij}(\mathbf{k})$, but the energy dependence of parameters $A_l(E)$ was neglected; all these parameters were taken at the free electron Fermi energy. Therefore our results far from the Fermi energy would be less meaningful.

Some results of our band structure calculations at the symmetry points of the Brillouin zone are shown in Table I. The way of calculating the Fermi energy ϵ_F is dealt with later.

From these data and Figs. 1 through 5 of our earlier paper[2] one can see the overlapping of the first and second bands, which is of the order of 0.1, 0.09, 0.04 Ry for Ca, Sr, and Ba, respectively, at atmospherical pressure, and becomes rapidly smaller with decreasing atomic volume.

Obviously, the Fermi energy ϵ_F must lie somewhere in the overlapping parts of the bands giving rise to electrons in the second Brillouin zone around the points L and to holes in the first zone around the points W and occasionally K and U.

It is remarkable to note that the ordering of energies at the points L and W remained unchanged, and although the overlapping became smaller with increasing pressure or in the series of metals Ca, Sr, and Ba, positive energy gap does not appear, because the crossing of energy curves Q_1 and Q_2 along the line WL is a necessary consequence of the ordering of these levels and the compatibility relations.

III. THE CONSTANT ENERGY SURFACES, THE FERMI ENERGY OF Ca, AND COMPARISON WITH EXPERIMENTS

Because of the strong similarities of the band structure of our three fcc metals we chose Ca as representative for the investigation of constant energy surfaces. Besides, experimental data for the shape of the Fermi surface are available,[4] to our best knowledge, only for Ca and this also indicates a theoretical estimation. The same secular Eq. (9) was used again in searching the energy contours, keeping the energy ϵ fixed and looking for those vectors **k** which satisfy this equation.

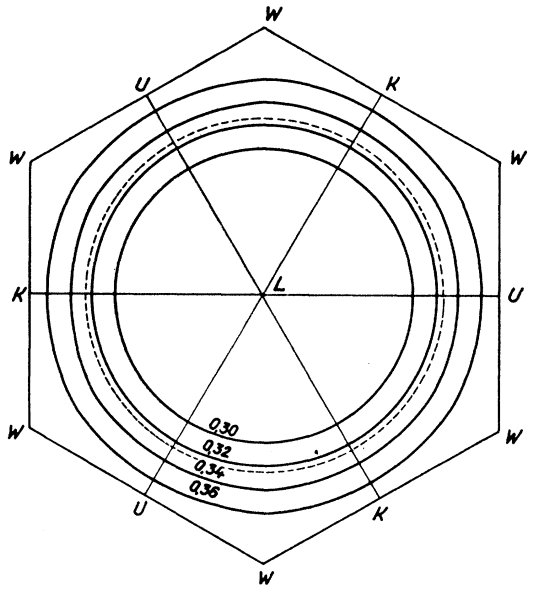

FIG. 1. Sections of constant-energy electron surfaces with the hexagonal face of the Brillouin zone for the fcc Ca. Energies in rydbergs and the broken line belongs to the free-electron Fermi surface. The curves are very nearly spherical with distortion not higher than 1%.

As it was mentioned we have electrons in the second zone and holes in the first one, and the volumes occupied by them in the first and second zones, respectively, must be equal to each other. This condition fits the Fermi energy ϵ_F. Figures 1 through 6 show sections of constant-energy surfaces.

From the pictures one can realize that, for energies smaller than 0.32 Ry measured from the bottom of the conduction band, one can find a connected hole surface in the first zone around the points W, K, and U. But for $\epsilon = 0.34$ Ry these surfaces became disconnected; the holes are located only around W. The crucial question is therefore whether the Fermi energy ϵ_F lies above or below the lowest energy at K. The first case leads to a "monster," as Harrison proposed,[5] while the second case gives rise to the dismembering of this monster into several pieces around the points W.

The extremal cross sections are presented on Fig. 7. If one accepts the experimental fact that there are only three measured de Haas–van Alphen (dHvA) periods, then one has to suppose the dismembering of Harrison's monster, otherwise too many nonobserved periods would be appearing. So the Fermi energy ϵ_F must be somewhere in the near vicinity of 0.33 Ry. Since the accurateness of our band structure calculations is surely no better than 0.01 Ry, we are not able to distinguish theoretically between the two models and the experi-

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

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

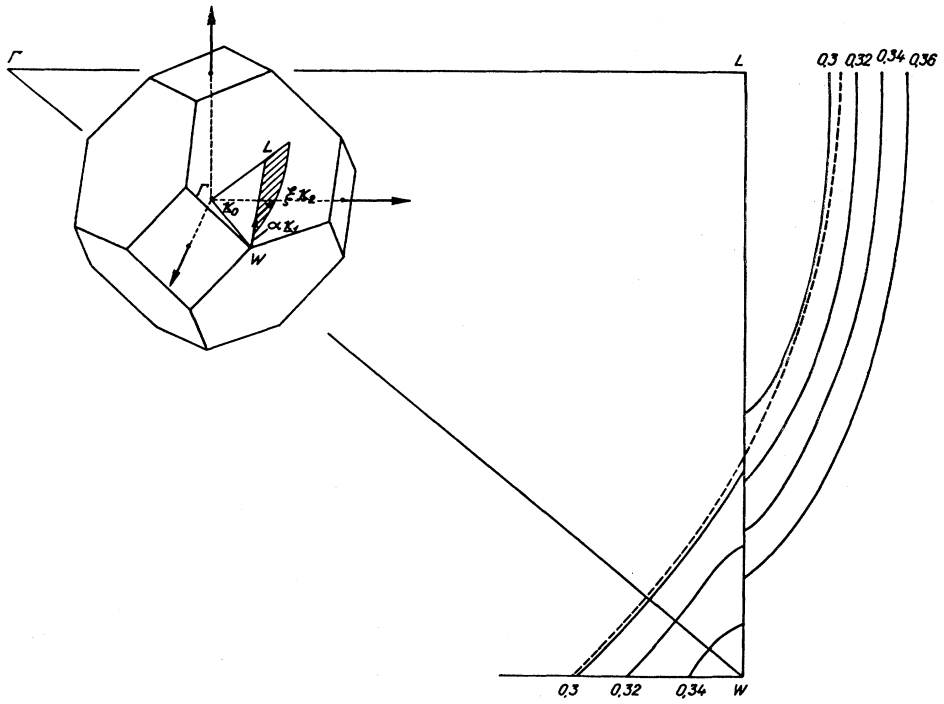

FIG. 2. Sections of constant energy electron surfaces with the plane ΓWL. The surfaces around L in the second Brillouin zone and around W in the first one belong to electrons and holes, respectively. The vectors κ_0, $\alpha\kappa_1$, and $\xi\kappa_2$ are indicating the way of calculations.

ment must decide whether there are holes around the points K or not. We have to mention the investigations of Altmann and Cracknell,[6] as well as that of Cracknell,[7] who also found holes around the points K, but not around the points W. Their results are much less free-electron-like than ours and gave a little too high dHvA periods, but as regards the number of periods, as well as the orientation dependence of them with respect to external face, they are quite consistent with the experimental data.[4] In our model as a best fit with the dHvA

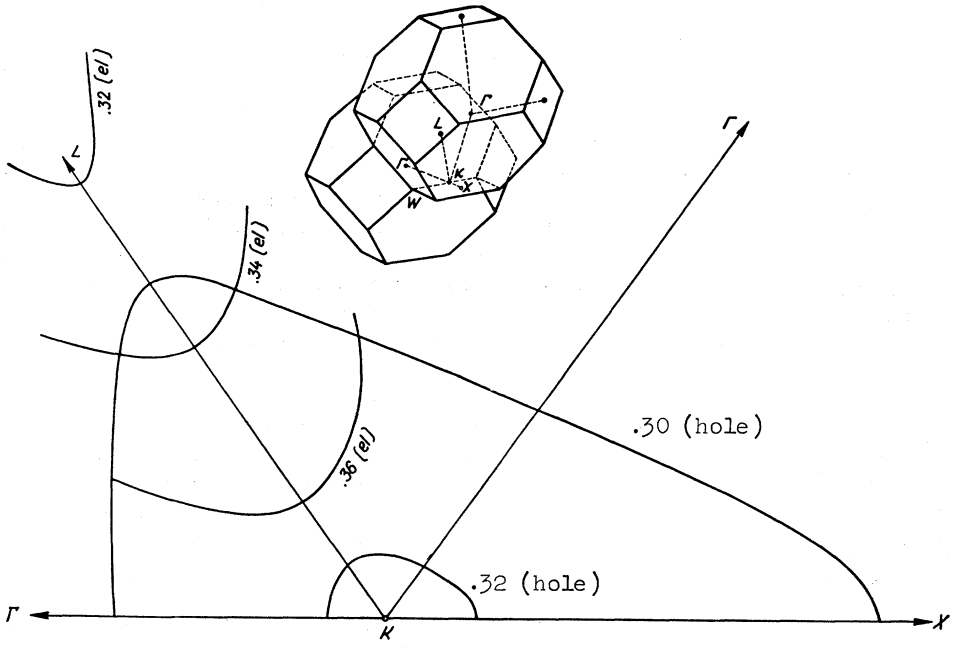

FIG. 3. Electron and hole surfaces on the plane ΓKL. Note that the hole surfaces are rapidly decreasing and nearly above 0.328 Ry, which is the lowest energy at K, are disappearing.

[6] S. L. Altmann and A. P. Cracknell, Proc. Phys. Soc. (London) **84**, 761 (1964).
[7] A. P. Cracknell, Phys. Letters **24A**, 263 (1967).

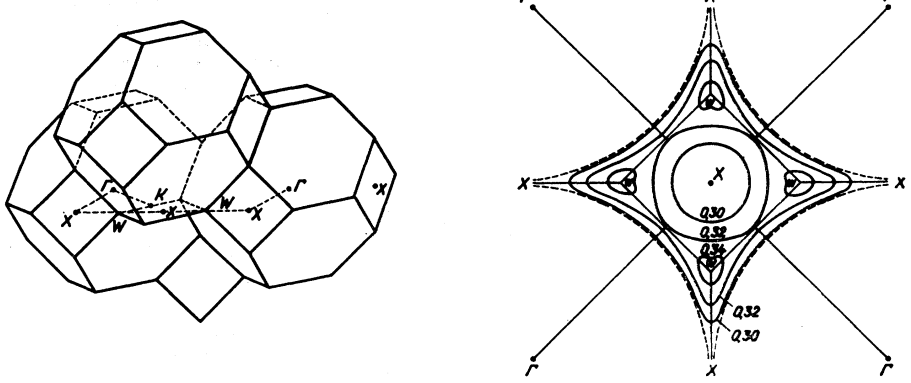

FIG. 4. Hole surfaces on the horizontal plane through the points ΓXW.

periods we arbitrarily take

$$\epsilon_F = 0.33 \text{ Ry}. \tag{10}$$

It is still more difficult to estimate the effect of the pressure on the shape of the Fermi surface. What seems to be sure is the decreasing tendency of the dimensions of our Fermi surface, which is an over-all consequence of the decreasing band overlapping or (negative) energy gap.

If one accepts a free-electron-like volume dependence of the Fermi energy, then one can suppose

$$\epsilon_F = 0.33(\Omega/\Omega_0)^{-2/3} \text{ Ry}. \tag{11}$$

This choice reserves the property that the Fermi energy is always above the lowest energy at K; therefore we do not expect any change in the *number* of the dHvA periods, but the numerical values of these periods must be rising because of the decrease of the dimensions of the Fermi surface. This assumption may be again the object of an experimental investigation. The same property seems to be valid in going from Ca to Sr and Ba. Numerical results for the dHvA periods and for the cyclotron effective masses are presented in Table II.

Summarizing, one can imagine the effect of increasing pressure on the shape of the Fermi surface as if the pressure were acting in the **k** space pushing back the electrons from the second zone into the first one fulfilling the holes around the corner points W.

In order to check the validity of our calculations by comparing with further experimental facts, we chose a simple model for our Fermi surface. (See Fig. 8.) The electron surface was replaced by spherical chalottes sitting on the hexagonal faces, the dimensions of which were easily interpolated immediately from our $\epsilon(\mathbf{k})$ curves along the line WL and ΓL. The pocket of holes was replaced by ellipsoids, this approximation being valid obviously in the case of dismembered hole surfaces.

On the basis of this simple model we calculated the electrical resistivity of absolutely pure Ca as a function of decreasing atomic volume.[3] The deformation potential method was used to estimate the electron–phonon matrix elements or rather the relaxation time τ.[8] This method is extremely suitable in our calculations, because the deformation parameters can be immediately calculated from the volume dependence of the electron energies at L and from the hole energies at W. The calculated resistivity at atmospheric pressure and room

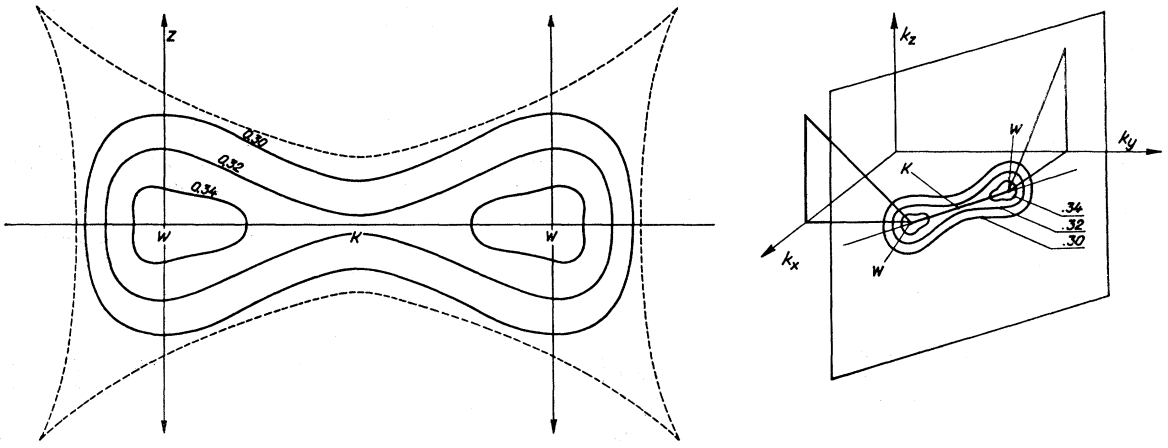

FIG. 5. Hole surfaces in the plane (1, 1, 0).

[8] J. Bardeen and W. Shockley, Phys. Rev. **80**, 72 (1950).

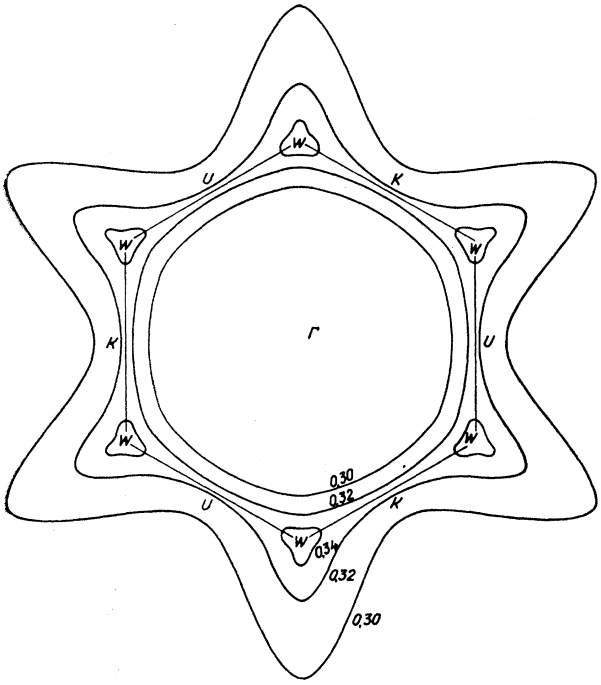

FIG. 6. Hole surfaces on the hexagonal (1, 1, 1) plane.

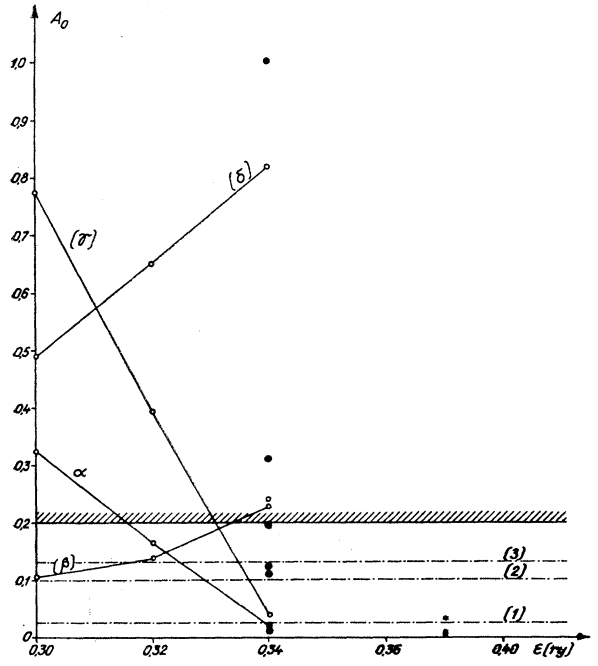

FIG. 7. Extremal areas of constant energy surfaces of the metal Ca at atmospheric pressure as functions of the energy parameter ϵ. The letters α, β, γ, δ refer to the Table II. The full circles are showing Harrison's results. The stars correspond to Altmann–Cracknell's results.[6] The horizontal lines are showing the experimental values.[4] The shadowed line corresponds to the upper limit of the experimentally investigated domain of periods. The ordinate is in units of $2\pi/a$.

TABLE I. The energy values of fcc metals Ca, Sr, and Ba in the symmetry points of the Brillouin zone at atmospheric pressures. Energies are given in rydbergs. Similar data concerning the relative atomic volumes of $\Omega/\Omega_0=0.9$, 0.8, 0.7, 0.6, 0.4 are available from the author by correspondence.

	Ca	Sr	Ba
$\Gamma_1(s)$	−0.0086	−0.0094	−0.0223
$\Gamma_{25}'(d)$	0.8961	0.8078	0.7345
X_1 (s, d)	0.2880	0.2575	0.1726
X_4' (p)	0.3500	0.3192	0.2802
X_3 (d)	0.4705	0.4282	0.2857
K_1 (s, p)	0.3276	0.2974	0.2215
K_3 (p, d)	0.3707	0.3377	0.2840
K_1 (s, p)	0.3853	0.3438	0.2555
W_2' (p, d)	0.3552	0.3216	0.2395
W_3 (d, p)	0.3872	0.3522	0.2799
W_1 (s, d)	0.5347	0.4692	0.3850
L_1 (s, d)	0.2362	0.2069	0.1376
L_2' (p)	0.2535	0.2336	0.2066
Fermi energy ϵ_F	0.3300		

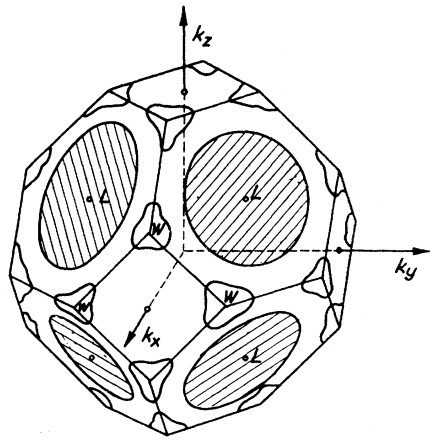

FIG. 8. The Fermi surface of Ca at atmospheridal pressure. The surface belongs to the Fermi energy $\epsilon_F=0.33$ Ry.

TABLE II. The de Haas–van Alphen periods and cyclotron masses. The former is given in the units of 10^{-7} G, the latter in units of the free electron. The directions of magnetic field H are also indicated. The letters α, β, γ, δ refer to Fig. 1.

	dHvA periods		Cyclotron masses	
Direction of H	Calc.	Exptl.	Calc.	Exptl.
(1, 1, 1) el. (α)	0.104		~1	
(1, 1, 0) el. (β)	0.45	0.57±5%	0.56	0.65±15%
(1, 0, 0) hole (γ)	0.34	0.77±5%	0.70	0.62±15%
(1, 1, 0) hole (δ)	0.69			
		3.05±2%		0.30±10%

temperature is $2.5\times10^{-6}\ \Omega$ cm, which reasonably agrees with the measured values of $4.0\times10^{-6}\ \Omega$ cm.[9] The decreasing dimensions of our Fermi surface give rise to the resistance increase showed by the experiment of Bridgman[10] and Stager and Drickamer.[11] The quantitative agreement of our numbers with these experimental results is reasonable up to about 300 kbar in the case of Ca.

Our simple model gives further numbers, too. The temperature coefficient of the low temperature specific heat for Ca at atmospheric pressure in comparison with the experimental value[12] is

$$\left.\begin{aligned}\gamma_{\text{calc}}&=2.8\\ \gamma_{\text{exptl}}&=1.78\end{aligned}\right\}\text{mJ/mole deg}^2.$$

The paramagnetic susceptibility is

$$\left.\begin{aligned}\chi_{\text{calc}}&=44.1\\ \chi_{\text{exptl}}&=19.9\end{aligned}\right\}10^{-6}\text{ erg/mole G}^2.$$

The calculated value of the thermal effective electron mass near the absolute zero temperature is $m_t=1.2$ free-electron mass. Further numbers as carrier concentrations and mobilities, the Hall coefficient, and estimations for ultrasound absorptions and magnetoresistance effects might be predicted in a similar sort of agreement with experiments as the numbers given above.

Instead of talking about the conclusions, we would rather say something about the failures of this model. First of all, it deals only with the fcc phase of these metals, although Ba is already bcc at atmospheric pressures. Secondly, we neglected the spin–orbit interaction which is allowed for the case of atmospheric pressure only. Since the shapes of the constant energy surfaces are very sensitive to the Fermi energy ϵ_F, likely beyond the accurateness of any sort of band structure calculations nowadays, our proposed shape of the Fermi surface must be further investigated experimentally. Experimental data for Sr and Ba would also be highly desirable. In a more accurate calculation one must take into account the energy dependence of the model potential parameters $A_l(E)$. One also might use a more precise method than this pseudopotential-like approximation was.

ACKNOWLEDGMENTS

The author is deeply indebted to the Steering Committee of the International Conference on Metal–Nonmetal Transitions for a travel grant making him able to participate in the conference, and personally to Professor J. C. Thompson for the kind hospitality during the author's stay in San Francisco.

[9] A. N. Gerritsen, *Handbuch der Physik*, S. Flügge, Ed. (Springer-Verlag, Berlin, 1956), Vol. **19**, p. 137.
[10] P. W. Bridgman, Proc. Am. Acad. Arts. Sci. **81**, 165 (1952).
[11] R. A. Stager and H. G. Drickamer, Phys. Rev. **131**, 2524 (1963).
[12] L. M. Roberts, Proc. Phys. Soc. (London) **B70**, 738 (1957).

Discussion of Vasvári's Paper

D. B. MCWHAN (Bell Telephone Laboratories): Figure 1 shows the resistivity as a function of temperature at different pressures for two samples of Sr. The calculations indicate that the number of carriers decreases with increasing pressure which is in agreement with the increase in the residual resistivity with increasing pressure. The calculated band structure suggests that Sr will never become a semiconductor in the face-centered cubic phase with increasing pressure because of an accidental degeneracy. Spin–orbit coupling could remove this degeneracy. The present experimental results are inconclusive on this point. Both samples are only 98–99 at. % Sr with resistivity ratios at 1 atm of 5 and 25 for samples 1 and 3, respectively. In sample 1 a negative temperature coefficient of resistivity is observed above 30 kbar but not in sample 3. Until purer Sr is available a definite answer cannot be given, but the present results suggest that Sr becomes a semimetal with increasing pressure in the fcc phase. On warming from 77°K at 46 kbar Sr transforms to a body-centered structure which is again a good metal as shown by the subsequent temperature cycle. This is also in agreement with the calculations of Vasvári *et al.*

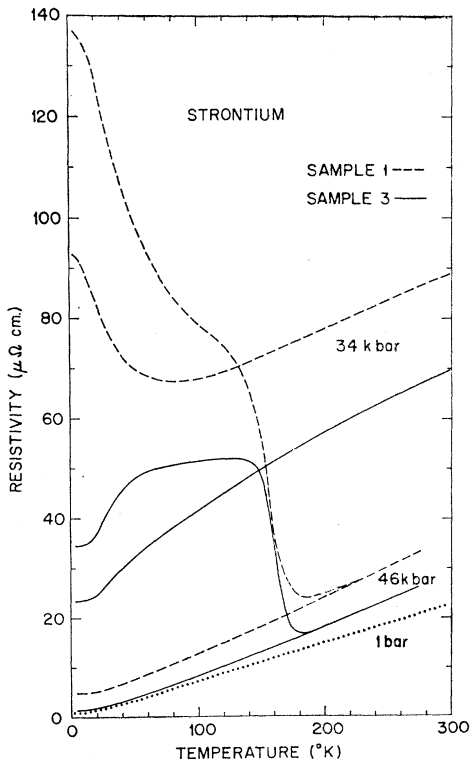

FIG. 1. The resistivity as a function of temperature at different pressures for two samples of Sr.