

## Electrical-resistance behavior of Ca at high pressures and low temperatures

K. J. Dunn and F. P. Bundy

*General Electric Company, Corporate Research and Development,  
Schenectady, New York 12301*

(Received 18 March 1981)

The electrical-resistance behavior of Ca is studied from 2 to 300 K at various pressures up to 440 kbar using a clamp-type sintered diamond-tipped opposed-anvil apparatus. It is found that the electrical resistance of Ca at room temperature increases monotonically as a function of pressure and reaches a maximum at about 180 kbar. With additional increase in pressure, the resistance of Ca decreases to a minimum around 250–300 kbar and then increases again sharply with a Ba-like up-jump at about 360 kbar and a second maximum around 420 kbar. Apparently, many first-order phase transformations in Ca have occurred at these high pressures. There is also a possibility for Ca to become superconducting at about 2 K and 440 kbar. No resistance anomalies at the low-temperature end were observed which might reflect the formation of an excitonic phase. The possibility of the nonexistence of the excitonic phase for Ca and the prediction of metal-semimetal-metal transition for Ca from the band calculations are discussed in light of the experimental findings.

### I. INTRODUCTION

In the conventional one-electron approximation at 0 K for crystalline solids, when the electronic-band overlap changes under the application of an external perturbation from positive to negative value, the number of free electrons and holes would decrease continuously to zero, and no anomalous electrical behavior would occur at the transition. Mott<sup>1</sup> first pointed out that this one-electron picture could not be correct in the neighborhood of the transition. He argued that, for a very small number of free carriers, electrons and holes would form bound pairs due to the attractive Coulomb potential, leading to an insulating state. Therefore, one should see a kink in the electrical resistivity as a function of temperature or pressure at the transition. Knox<sup>2</sup> later studied the same problem in an insulator and remarked that if the exciton binding energy  $|E_B|$  exceeded the indirect band gap  $|E_G|$  the conventional insulating ground state would be unstable against the formation of excitons. Jérôme *et al.*<sup>3</sup> and Halperin and Rice<sup>4</sup> had suggested a number of materials as possible candidates for realizing the excitonic phase. These are the materials which under normal conditions have a small (positive or negative)

gap that can be varied continuously through zero by some external means without the occurrence of a polymorphic transition. This list includes Ca, Sr, Yb, I, and other less likely semimetals in group Va. McWhan *et al.*<sup>5</sup> measured the electrical resistivity of Sr and Yb from 2 to 298 K at different pressures up to 50 kbar. No anomalies were observed which could be associated with the formation of an excitonic phase. Dunn and Bundy<sup>6</sup> studied the electrical behavior of molecular iodine in the neighborhood of the band overlap. No resistance anomalies were found in the low-temperature limit, either. Calcium remained to be explored.

The electrical properties of calcium are also interesting from the point of view of electronic-band-structure calculation. Since Stager and Drickamer's work on Ca,<sup>7</sup> in which they reported a maximum in the resistance at a pressure of about 350 kbar (according to the pressure scale in use at the time, 1963) and observed that it appeared to behave as a semimetal or semiconductor between 77 and 300 K over a range of pressure in the region of the resistance maximum, there have been many band-structure calculations on Ca.<sup>8–15</sup> Each of them predicts different onset pressures (or volume compressions) for metal-semimetal and semimetal-

metal transitions in Ca, none of which agrees with existing experimental data.

In the present paper, we report measurements of the electrical resistance of Ca from about 2 to 300 K at various pressures up to 440 kbar. A search was made at low temperatures for the excitonic phase, but the result was negative. We find that the electrical resistance of Ca at room temperature increases as a function of pressure and reaches a maximum at about 180 kbar. A similar maximum was reported by Stager and Drickamer<sup>7</sup> around 350 kbar in an old pressure scale. Interestingly enough, with additional increase in pressure, the resistance of Ca decreases to a minimum around 250–300 kbar and increases again sharply with an up-jump (similar to Ba at 58 kbar) at about 360 kbar and a second maximum around 420 kbar. Apparently, many first-order transformations in Ca have occurred at these high pressures. The electrical behavior of Ca at low temperature and high pressures (below 200 kbar) is consistent with the predictions of the previous band calculations that Ca remains semimetallic in an fcc phase.

## II. EXPERIMENTAL

The pressure equipment used in this investigation is the cryogenic clamp-type sintered diamond-tipped opposed-anvil apparatus. The details of the design and experimental procedure have been described in Ref. 16 and the method of pressure calibration in Ref. 17.

Calcium metal, in the form of turnings, was obtained from Allied Chemical Corporation. Elemental analysis indicates that it contains about 0.028 wt. % Sr and 0.019 wt. % Fe. All other impurities are less than 100 ppm.

The samples were prepared under white oil by rolling freshly cut Ca metal chips with a tungsten carbide scriber to form thin foils about 0.03 mm thick. From these thin foils, specimens of rectangular shape of about  $0.13 \times 0.6 \text{ mm}^2$  were cut and placed in the high-pressure cell in contact with gold electrodes. Figure 1 shows the arrangement of the specimen, electrodes, and sample holder in the high-pressure cell. Because the sintered diamond compact tips are not good electrical conductors, there are two 0.050-mm-diameter tungsten wires on each side of the pyrophyllite gasket bridging the gold electrodes to the carbide part of the pistons. The resistance of the sample was monitored by sending through an exciting current and measuring the voltage drop across the pistons. The back-

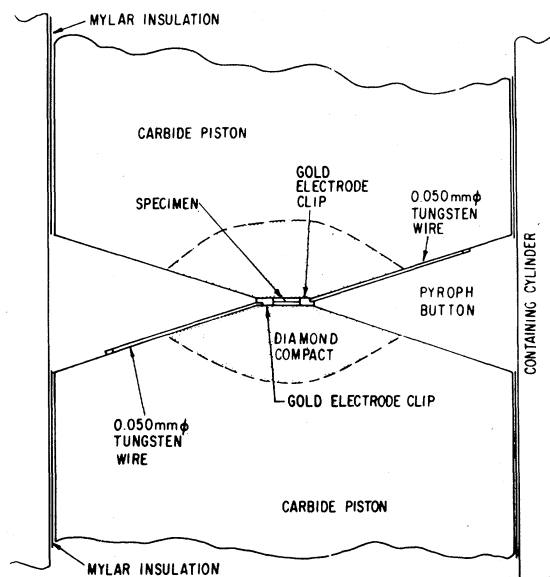


FIG. 1. Sectional view of the arrangement of the specimen, electrodes, and sample holder in the high-pressure cell.

ground electrode resistance which mainly came from the resistance of the bridging tungsten wires, contributing about  $0.17 \Omega$  at 300 K and  $0.02 \Omega$  at liquid-helium temperatures, was subtracted from the total resistance to obtain the sample resistance.

Figure 2 shows a typical result of electrical resistance versus pressure for Ca at room temperature up to about 340 kbar. An approximate cell-pressure scale, which applies only to the loading curve, is also indicated. The initial decrease in resistance is due to the firming of electrical contacts and the settling of the pyrophyllite gasket. As shown in Fig. 2 at the low-pressure end, Bridgman's data<sup>18</sup> on Ca is also plotted as a dashed line joining our curve smoothly. This was done by taking Bridgman's data in a modified pressure scale from Ref. 19, assuming  $R/R_0$  ( $R_0$  is the resistance at zero pressure) at 80 kbar to be 6, and adjusting the pressure scale further from 80 to 72 kbar.<sup>20</sup> At higher loadings, the resistance of the sample becomes dominant and increases as a function of pressure. It reaches a maximum at 180 kbar, drops to a minimum around 250–300 kbar, and increases sharply beyond that. Previous work by Stager and Drickamer,<sup>7</sup> limited by the strength of the carbide anvils, was done up to around 220 kbar. Combining the results of Bridgman and ours, we estimate that the resistance of Ca at 180 kbar increases by a factor of approximately 50 from that at atmospheric pressure.

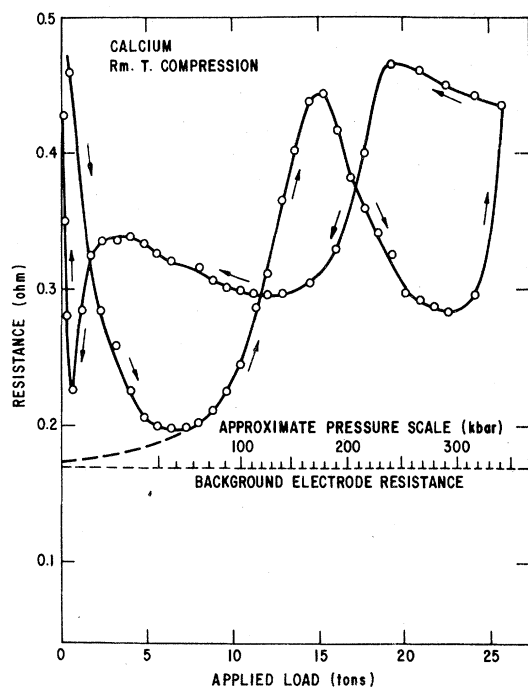


FIG. 2. Electrical resistance of Ca versus pressure at room temperature. The approximate cell-pressure scale applies to the loading curve only.

In one of the cryogenic runs, the pressure was increased to almost 440 kbar, the highest of all our runs. The loading and unloading resistance versus pressure curves at room temperature, shown in Fig. 3, reveal even more interesting and surprising features in Ca at high pressures. At 360 kbar, there is a jump in the  $R$  vs  $P$  curve, indicating an intermediate phase. Beyond that, the resistance of Ca rises rapidly, reaches a second maximum at 420 kbar, and starts tapering off, apparently transforming to another phase. All these features were reproduced in the unloading curve. Summarizing the information obtained from the  $R$  vs  $P$  curve for Ca and combining the analysis which we will discuss later, we believe that Ca remains in the fcc phase up to pressures around 210 kbar, transforms to a new phase (III) in the 210–300 kbar region, changes to an intermediate phase (IV) at 300–360 kbar, and becomes yet another phase (V) beyond 360 kbar for pressures up to 440 kbar.

Figure 4 shows the results of resistance versus temperature for Ca of various isobaric runs. These runs were done by loading the sample in the clamp press at room temperature, inserting the clamped rig into a cryogenic Dewar, lowering the temperature to

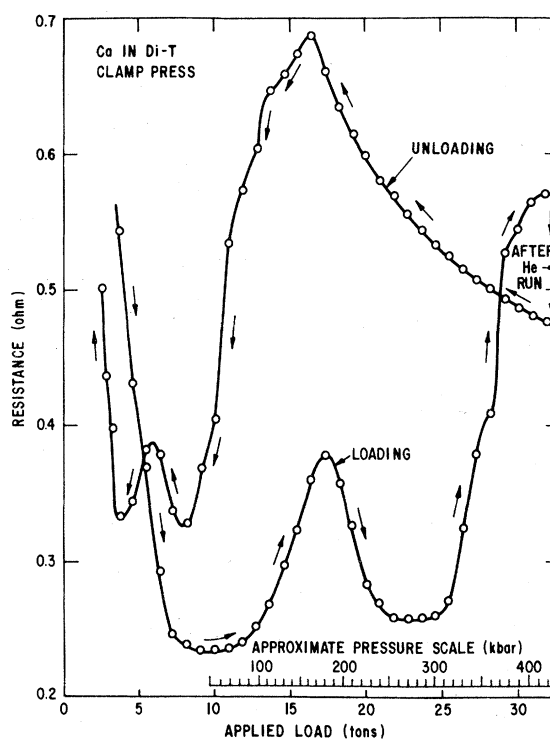


FIG. 3. Loading and unloading resistance versus pressure curves for Ca at room temperature in the clamp press. The approximate cell-pressure scale applies to the loading curve only.

liquid-helium temperatures and below, and monitoring the resistance of the sample during the slow warm-up. The clamp press, designed to be temperature compensated, gives nearly constant cell pressure during the slow warm-up process. In the runs with pressures of 62, 80, and 98 kbar, we used the tungsten carbide anvil apparatus rather than the diamond-tipped anvils with samples of the same thickness and twice the length and the width of the regular samples. The area-length ratio of the sample in every run is approximately the same (within 20%). Therefore, it is significant and instructive to construct "synthetic" isothermal  $R$  vs  $P$  curves from the curves shown in Fig. 4 by reading resistance values along a constant-temperature axis. Such "synthesized" isothermal  $R$  vs  $P$  curves are shown in Fig. 5. It is interesting to note that the room-temperature curve (solid line) in Fig. 5 is quite similar to that shown in Fig. 2. The agreement is excellent considering the error involved in subtracting the background electrode resistance, the slight nonuniformity in sample sizes, and the unknown distortion of sample geometry at high pressures.

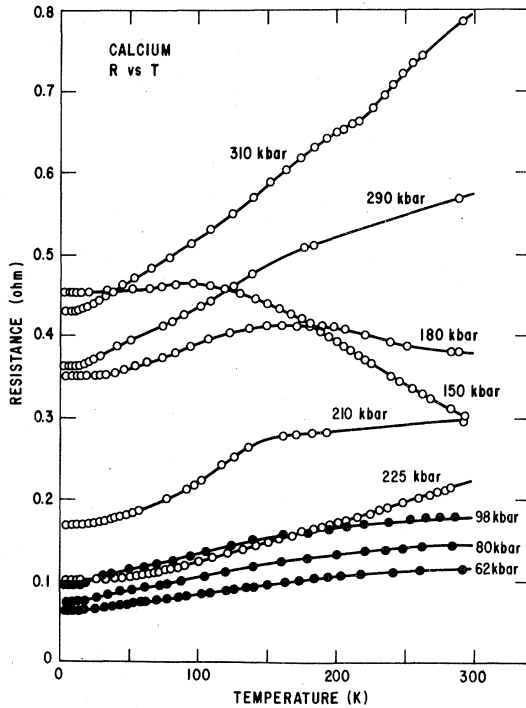


FIG. 4. Resistance versus temperature curves for Ca at various fixed cell pressures.

In Fig. 4, we note that the temperature coefficient  $dR/dT$  is quite small for pressure at 62, 80, and 98 kbar and becomes negative near room temperature for pressures at 150 and 180 kbar. These features are reflected more clearly in Fig. 5, noting that  $dR/dT$  is negative between 100 and 300 K in the 120–190 kbar region, and is positive below 120 and above 190 kbar. These constructed isothermal curves are more informative in other aspects: They show (i) that the first resistance peak at 180 kbar at room temperature shifts toward lower pressure as the temperature is lowered and reaches 155 kbar at 4.2 K, and (ii) that there is a possibility, noting the change in  $dR/dP$  of these curves near 310 kbar, that the up-jump in the resistance which occurred at 360 kbar at room temperature might happen at a lower pressure for lower temperatures. These imply that  $dP/dT$  along the phase boundaries fcc-III and IV-V are positive for temperatures below 300 K.

Based on the above information, we can construct a tentative phase diagram for Ca as shown in Fig. 6. The melting curve and the phase line between fcc and bcc determined by Jayaraman *et al.*<sup>21</sup> are also shown in the diagram. For convenience, we designate the fcc and bcc phases as I and II, respectively,

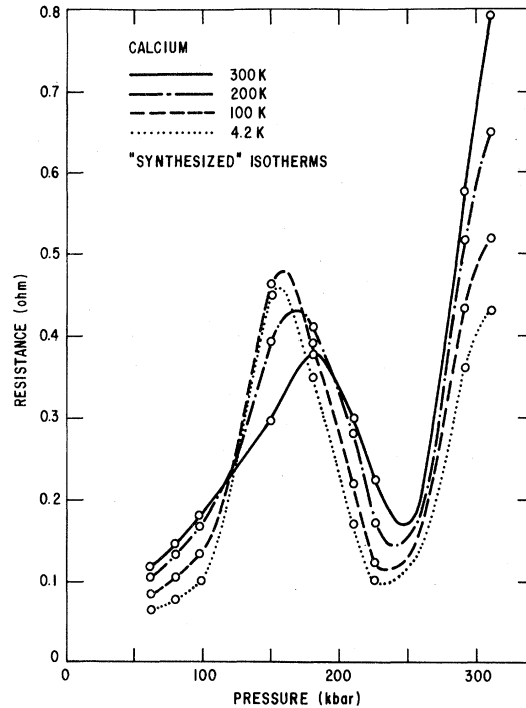


FIG. 5. "Synthesized"  $R$  vs  $P$  isothermal curves for Ca.

and the remaining unknown phases as III, IV, and V. The phase boundary between phases I and III is represented by a shaded band because of the inability to locate the precise transition pressure. The lower bound of the shaded band is the locus of the first resistance peak. The upper bound is the locus of the predicted critical pressure at which the band overlap is equal to zero. This will be discussed later in further detail. There is evidence, also presented later, that the electronic band structure is quite different between phases I and III. Whether this is a band-structure change or a crystallographic structural change is not determined. A complete and thorough x-ray diffraction study at high pressures would be most helpful in this connection. The shock-compression work by Bakanov and Dudoladov<sup>22</sup> indicates an abrupt decrease in the compressibility at around 400 kbar. Assuming a 10% correction at this pressure from Hugoniot to isothermal, we believe this change may be related to the IV to V transition suggested above.

Figure 7 shows the  $R$  vs  $T$  curve for Ca of the isobaric run at almost 440 kbar. The enlarged  $R$  vs  $T$  behavior at the low-temperature limit shown in the inset indicates a tendency for Ca to transform to

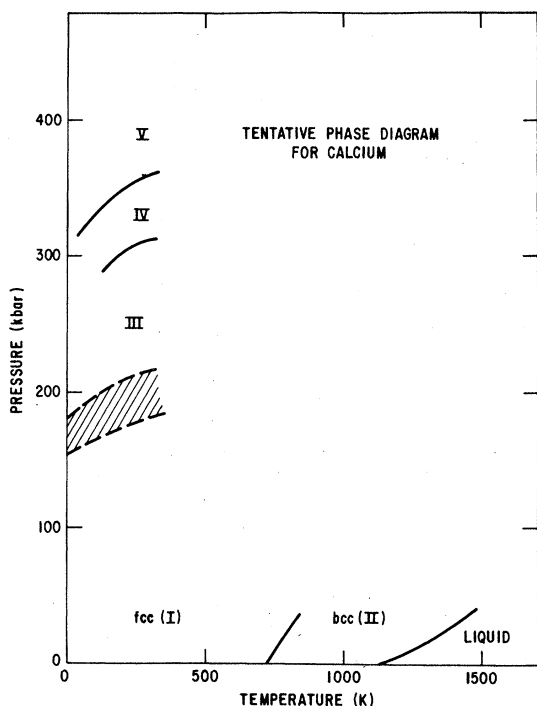


FIG. 6. Tentative phase diagram for Ca.

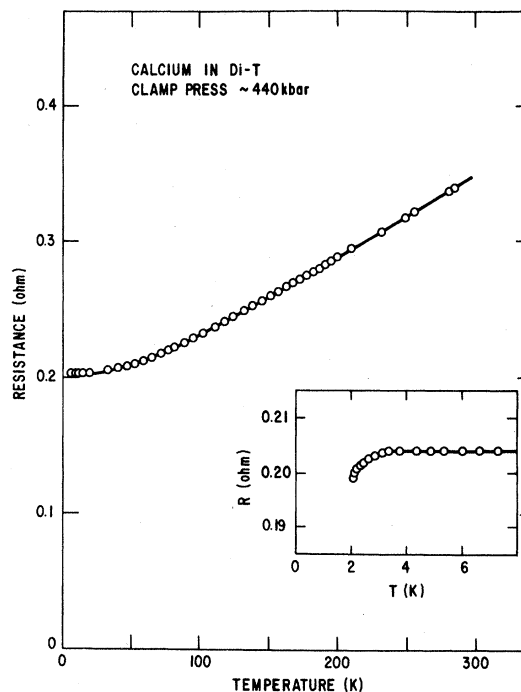
a different state (possibly a superconducting state) near 2 K (which is a current limit of our apparatus). From the similarity in the  $R$  vs  $P$  behavior for Sr and Ca and for Ba and Ca (above 250 kbar), one is tempted to suggest that phase III of Ca may be bcc and that phases III and IV of Ca may also become superconducting at temperatures considerably lower than 2 K, possibly in the millidegree region. Further measurements at temperatures much lower than 2 K and at pressures higher than 250 kbar will be required to test this hypothesis.

### III. DISCUSSION

#### A. Excitonic phase

As shown in Fig. 4, no anomalies in resistance behavior for Ca were observed in the low-temperature limit of the isobaric runs. In most of these runs, the temperature was lowered to 2.3 K; in some cases, only to 4.2 K.

To investigate at what pressures we should be looking for the excitonic phase, we consider the variation of resistance with pressure and temperature in a simple two-band model. Balla and

FIG. 7.  $R$  vs  $T$  curve for Ca at about 440 kbar. The insert shows the  $R$  vs  $T$  behavior in the low-temperature region.

Brandt<sup>23</sup> have shown for Bi that this model gives a value for  $P_c$ , the critical pressure at which band overlap is equal to zero, in good agreement with the Schubnikov-de Haas effect predictions.<sup>24</sup> In the liquid-helium temperature region, the residual resistance  $R_0$  is inversely proportional to the charge carrier density  $n_0$ . The constructed  $R$  vs  $P$  isothermal curve at 4.2 K (dotted line) shown in Fig. 5 reflects quantitatively the effect of compression on the carrier density  $n_0$  for Ca. Near the band crossing, one may expand  $|E_G|$ , the band overlap energy, in a power series of  $1 - P/P_c$ . In the first-order approximation, we have

$$|E_G| = \alpha(1 - P/P_c). \quad (1)$$

Assuming a quadratic-dispersion law, we have  $n_0(P) \propto |E_G|^{3/2}$ , so that

$$n_0(P) \propto R_0(P)^{-1} = \beta(1 - P/P_c)^{3/2}. \quad (2)$$

Using a least-squares method, we fit the residual resistance value of Ca at pressures of 62, 80, 98, and 150 kbar with Eq. (2) and obtain  $P_c = 180.6$  kbar and  $\beta = 31.7$ . The result is shown in Fig. 8. Taking the theoretical value of band-overlap energy at zero pressure from the work by Altmann

*et al.*,<sup>12</sup> i.e.,  $|E_G| = 0.06$  Ry, we also plot Eq. (1) in Fig. 8.

In their article about excitonic insulators, Jérôme *et al.*<sup>3</sup> estimate the exciton-binding energy  $|E_B|$  for Ca to be

$$|E_B| = 4 \times 10^{-3} \text{ eV (or } 2.9 \times 10^{-4} \text{ Ry)} \quad (3)$$

and the transition temperature  $T_c$  to the excitonic phase to be

$$T_c = 20 \text{ K} . \quad (4)$$

The pressure range  $\Delta P$  over which the excitonic phase might be observed is given by

$$\Delta P = \left[ \frac{\partial |E_G|}{\partial P} \right]^{-1} |E_B| . \quad (5)$$

Substituting  $|E_G| = 0.06$  Ry,  $P_c = 180.6$  kbar, and  $|E_B| = 2.9 \times 10^{-4}$  Ry we obtain

$$\Delta P = 0.9 \text{ kbar} . \quad (6)$$

From the above estimates, we learn that the excitonic phase of Ca (if it exists) might be observed only in a very small pressure region near  $P_c = 180.6$  kbar. Although this pressure number is stated to four significant figures, it must be recognized that in both experiment and theory, the absolute accuracy is probably no better than  $\pm 5$  kbar.

Experimentally, it seems the band structure has changed (possibly due to a first-order phase transformation) before the critical-pressure region is reached. If the change of band overlap were to continue according to Eqs. (1) and (2), the residual resistance  $R_0$  would have kept increasing after 150 kbar. As shown in Fig. 5, the residual resistance

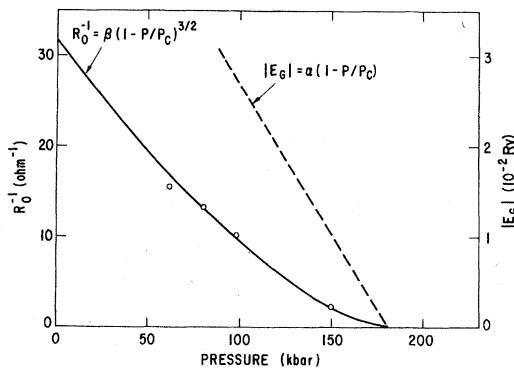


FIG. 8. Fitted curve of  $R_0^{-1} = \beta(1 - P/P_c)^{3/2}$  using a two-band model. The equation  $|E_G| = \alpha(1 - P/P_c)$  is also plotted assuming  $|E_G|$  at zero pressure to be 0.06 Ry.

$R_0$  at 4.2 K reaches a maximum at 155 kbar and starts decreasing again, indicating a major change in the band structure. Figure 9 shows a plot of ideal resistance,  $R_T = R(\text{total}) - R_0$  (residual), versus temperature for different pressures from 60 up to 310 kbar in logarithmic scale. The results of runs at 150 and 180 kbar were not plotted because the  $R_T$  was too small for us to obtain a meaningful curve. We can see in Fig. 9, assuming a form  $R_T \propto T^n$ , that  $n$  is approximately 1.8 for runs at 62, 80, and 98 kbar and becomes slightly larger than 3 for runs at 210 and 225 kbar. This strongly suggests that a polymorphic transformation has taken place. There are band calculations for Ca predicting that it undergoes a metal-semimetal-metal transition in the fcc phase; however, the pressure range involved in the transition is much broader than what we found here. Therefore, we believe there is a phase transformation in Ca occurring at pressure between 155 and 180 kbar at 4.2 K and at pressures between 180 and 210 kbar at 300 K. This is the reason why we have shown a  $P, T$  band rather than a line in the phase diagram in Fig. 6.

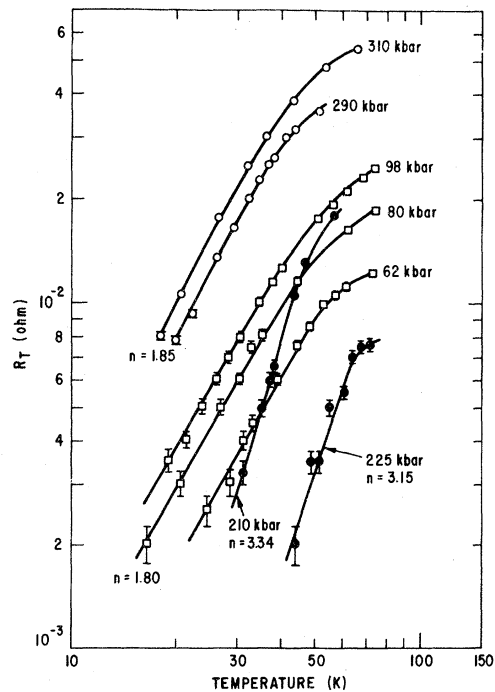


FIG. 9. Ideal resistance  $R_T$  of Ca versus temperature at different pressures. Assuming a form of  $R_T \propto T^n$ , we obtain the approximate value of  $n$  for different pressures.

If the above analysis is true, the excitonic phase of Ca might not exist at all. Of course, uncertainties were involved in the estimates of  $|E_B|$ ,  $P_c$ ,  $\Delta P$ , the transition pressure from phases I to III, etc. No definitive statement can be made about the nonexistence of the excitonic phase for Ca at this moment.

### B. Band structure

Most of the people who calculated the band structure for Ca compared their results with the experimental data obtained by Stager and Drickamer.<sup>7</sup> Because the experimental pressure scale has been modified since then, some of the conclusions drawn from such a comparison become irrelevant now.

For the convenience of discussion, we show in Fig. 10 the early  $PV$  data for Ca by Bridgman<sup>25</sup> and extrapolate them to 500 kbar using the first-order Murnaghan equation [curve (a)]. Curve (b) is obtained by fixing  $B_0$ , the isothermal bulk modulus for Ca at zero pressure, and adjusting  $B'_0$ , the first pressure derivative of  $B_0$  at zero pressure, in such a way that the compression which corresponds to 88 kbar on curve (a) will give 75 kbar on curve (b). Such a modification in the pressure scale is made because the transition pressure of Bi V-VII thought to be 88 kbar at that time is now modified to 75 kbar.

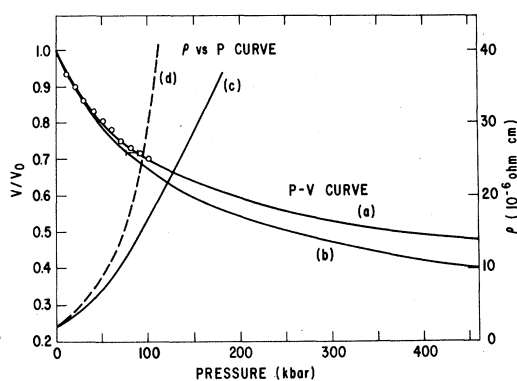


FIG. 10.  $V$  and  $\rho$  vs  $P$  curves for Ca. Curve (a) is obtained by using Bridgman's  $PV$  data for Ca fitted with the first-order Murnaghan equation. Curve (b) is obtained from curve (a) by fixing  $B_0$  and adjusting  $B'_0$  such that the compression corresponding to 88 kbar on curve (a) becomes 75 kbar on curve (b). Curves (c) and (d) are the theoretical and "experimental"  $\rho$  vs  $P$  curves for Ca, respectively.

Most of the band calculations for Ca in the fcc structure indicate similar features about the Fermi surface, with electrons around  $L$  and holes around  $W$ , which shrinks with decreasing volume (see, for instance, Ref. 10). The strong  $d$ -band coupling near the Fermi level and the symmetry requirements in the fcc phase result in a line of degeneracy between the first and second bands, so that the material can become only a semimetal but not a semiconductor. These theoretical conclusions are consistent with our experimental findings (below 200 kbar) that the resistance of Ca did not increase exponentially as the temperature decreased. Vasvari and Heine<sup>9</sup> calculated the resistivity  $\rho$  vs Ca in the fcc phase as a function of volume at room temperature. Their  $\rho$  vs  $P$  result is plotted as curve (c) in Fig. 10 [using the  $PV$  curve (b) shown in Fig. 10]. For comparison, our experimental result is plotted as  $\rho$  vs  $P$  also [curve (d)], assuming the same resistivity value at zero pressure. One notices the "experimental" resistivity rises much faster with increasing pressure than the theoretical one.

Vasvari *et al.*<sup>10</sup> predicted a metal-semimetal transition at  $V/V_0 = 0.55$  where the Fermi surface practically vanished. This  $V/V_0$  corresponds to a pressure<sup>26</sup> of 192 kbar which is quite close to our critical pressure  $P_c$  of 180 kbar (i.e.,  $V_c/V_0 = 0.56$ ). Vasvari *et al.*<sup>10</sup> also calculated the band structure for Ca in the bcc phase. As shown in Fig. 6 of Ref. 10, when  $V/V_0$  decreases, the gap at  $N$  opens up and  $H_{12}$  drops in energy relative to  $P_4$ . We, therefore, expect Ca in the bcc phase to be a metal at all pressures, though the Fermi surface would be very small when  $H_{12}$  is at the same energy as  $P_4$ . This critical volume [i.e., where  $E(H_{12}) = E(P_4)$  for bcc Ca] at which there may be a resistance maximum is estimated to be  $V/V_0 = 0.7$ . If the bulk modulus for bcc Ca is not too much different from that for fcc Ca, the compression  $V/V_0 = 0.7$  corresponds to a pressure of 85 kbar, far below the critical pressure  $P_c$  of 180 kbar. This means that phase III for Ca, if it is bcc, should have normal electrical resistance behavior versus pressure, i.e.,  $R$  decreases monotonically with  $P$  without the occurrence of a maximum. However, experimentally, we observe that  $R$  increases again beyond 300 kbar as shown in Fig. 3. This must be due either to the occurrence of a phase transformation (III-IV) or to a change in the band structure of phase III which is not bcc and has a Fermi surface that shrinks for higher pressure. If the latter is true, III and IV will actually be one phase.

Altmann *et al.*<sup>11</sup> treated the rise in resistance of

Ca at around 100 kbar (or 140 kbar in the old scale) as the onset of metal-semimetal transition, which, in our opinion from the analysis of the residual resistance  $R_0$  vs  $P$ , should be around 180 kbar near the resistance peak. The values of Altmann *et al.* of  $V_c/V_0 = 0.84$  (or 33 kbar) using a Slater-type potential<sup>11</sup> and their later value of  $V_c/V_0 = 0.68$  (or 95 kbar) using a  $k$ -dependent potential<sup>12</sup> are both too far from our experimental value of  $V_c/V_0 = 0.56$  (or 180.6 kbar). Both McCaffrey *et al.*<sup>13</sup> and Mickish *et al.*<sup>14</sup> predicted a metal-semimetal-metal ( $M$ - $S$ - $M$ ) transition for Ca in the fcc phase. McCaffrey *et al.*<sup>13</sup> obtained a volume compression for the  $M$ - $S$  transition as  $V_c/V_0 = 0.804$  (or 42 kbar) and that for the  $S$ - $M$  transition as  $V_c/V_0 = 0.512$  (or 242 kbar), whereas Mickish *et al.*<sup>14</sup> obtained  $V_c/V_0 = 0.55$  (or 192 kbar) and  $V_c/V_0 = 0.38$  (or 500 kbar), respectively. Apparently, the large pressure range covered by the  $M$ - $S$ - $M$  transition (especially  $S$ - $M$ ) is not consistent with our experimental results.

#### IV. CONCLUSIONS

Summarizing our findings and discussion, we have the following conclusions:

(1) Ca, at room temperature, remains in the fcc phase up to pressures of 180–210 kbar, transforms to a new phase (III) in the 210–300 kbar region, changes to an intermediate phase (IV) in the 300–360 kbar region, and becomes yet another phase (V) beyond 360 kbar and up to 440 kbar.

(2) There is a possibility for Ca to become superconducting at 440 kbar near 2 K.

(3) The critical pressure  $P_c$  at which the band overlap energy is zero is estimated to be around 180.6 kbar.

(4) The excitonic phase might not exist for Ca.

(5) Some of the predictions of the band calculations for Ca on the metal-semimetal transition are consistent with our experimental results. However, for pressures higher than the semimetal region, a semimetal–new-phase (III) transition seems more plausible than a semimetal-metal transition for Ca remaining in an fcc phase.

#### ACKNOWLEDGMENTS

The authors wish to thank Dr. M. Aven and Dr. A. W. Urquhart for supporting this research.

- 
- <sup>1</sup>N. F. Mott, *Philos. Mag.* **6**, 287 (1961).  
<sup>2</sup>R. S. Knox, *Theory of Excitons*, Suppl. 5 of *Solid State Physics* (Academic, New York, 1963), p. 100.  
<sup>3</sup>D. Jérôme, T. M. Rice, and W. Kohn, *Phys. Rev.* **158**, 462 (1967).  
<sup>4</sup>B. I. Halperin and T. M. Rice, in *Solid State Physics* edited by H. Ehrenreich, F. Seitz, and D. Turnbull, (Academic, New York, 1968), Vol. 21, p. 115.  
<sup>5</sup>D. B. McWhan, T. M. Rice, and P. H. Schmidt, *Phys. Rev.* **177**, 1063 (1969).  
<sup>6</sup>K. J. Dunn and F. P. Bundy, *J. Chem. Phys.* **72**, 2936 (1980).  
<sup>7</sup>R. A. Stager and H. G. Drickamer, *Phys. Rev.* **131**, 2524 (1963).  
<sup>8</sup>W. A. Harrison, *Phys. Rev.* **131**, 2433 (1963).  
<sup>9</sup>B. Vasvari and V. Heine, *Philos. Mag.* **15**, 731 (1967).  
<sup>10</sup>B. Vasvari, A. O. E. Animalu, and V. Heine, *Phys. Rev.* **154**, 535 (1967).  
<sup>11</sup>S. L. Altmann, R. C. Harford, and R. G. Blake, *J. Phys. F* **1**, 791 (1971).  
<sup>12</sup>S. L. Altmann, R. C. Harford, and R. G. Blake, *J. Phys. F* **2**, 1062 (1972).  
<sup>13</sup>J. W. McCaffrey, J. R. Anderson, and D. A. Papaconstantopoulos, *Phys. Rev. B* **7**, 674 (1973).  
<sup>14</sup>D. J. Mickish, A. B. Kunz and S. T. Pantelides, *Phys. Rev. B* **10**, 1369 (1974).  
<sup>15</sup>R. A. Ballinger and B. R. Allen, *J. Phys. F* **5**, 1135 (1975).  
<sup>16</sup>F. P. Bundy and K. J. Dunn, *Rev. Sci. Instrum.* **51**, 753 (1980).  
<sup>17</sup>K. J. Dunn and F. P. Bundy, *Rev. Sci. Instrum.* **49**, 365 (1978).  
<sup>18</sup>P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **81**, 165 (1952).  
<sup>19</sup>F. P. Bundy and H. M. Strong, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1962), Vol. 13., p. 81.  
<sup>20</sup>The adjustment from 80 to 72 kbar was obtained with the help of the  $PV$  curves (a) and (b) for Ca shown in Fig. 10.  
<sup>21</sup>A. Jayaraman, W. Klement, Jr., and G. C. Kennedy, *Phys. Rev.* **132**, 1620 (1963).  
<sup>22</sup>A. A. Bakanov and I. P. Dudoladov, *Zh. Eksp. Teor. Fiz. Pis'ma Red.* **5**, 322 (1967) [*JETP Lett.* **5**, 265 (1967)].  
<sup>23</sup>Balla and Brandt, *Zh. Eksp. Teor. Fiz.* **47**, 1653 (1964) [*Sov. Phys.—JETP* **20**, 1111 (1965)].  
<sup>24</sup>E. L. Itskevich and L. M. Fisher, *Zh. Eksp. Teor. Fiz.* **53**, 98 (1967) [*Sov. Phys.—JETP* **26**, 66 (1968)].  
<sup>25</sup>P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **74**, 425 (1942).  
<sup>26</sup>This is done by using the  $PV$  curve (b) in Fig. 10. All the conversions of  $V/V_0$  to  $P$  in the following discussion are done in the same way.