# Effect of Temperature and Pressure on the Electrical Resistance of Four Alkaline Earth Metals*

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The resistance of magnesium, calcium, strontium, and barium have been measured to 600 kbar at temperatures from 77 to 296°K.

Magnesium shows some shallow maxima and minima in resistance along an isotherm, but no striking features. Calcium has a phase transition at about 150 kbar to a semimetallic phase, and a second transition initiating near 300 kbar, to a metallic state. Strontium has a sharp maximum in resistance below 40 kbar. Near the maximum it may be a semimetal. There is then a phase transition to metallic phase.

Barium exhibits a very sharp rise in resistance at 140 kbar at 296°K (190 kbar at 197°K). At 77°K there is a transition at 240 kbar which is somewhat more sluggish. Isobars obtained on this high-pressure phase indicate a very sharp transition near 160°K. The evidence indicates that barium is a liquid at high pressure above 160°K.

THE effect of pressure and temperature has been measured on the resistance of magnesium, calcium, strontium, and barium. The pressure range was to 600 kbar or more. Isotherms were obtained at 296 and 77°K. Isobars were also obtained at various pressures by heating at a controlled rate from 77 to 296°K.

The general features of the high-pressure technique have been previously described.[1,2] Since some of these materials are quite reactive, the AgCl pressure transmitting "fluid" was replaced by naphthalene. Appropriate checks on the pressure calibration were made. Samples were prepared and loaded in an atmosphere of dried argon to minimize reaction with oxygen or water vapor. The sources and purity of the various materials are shown in Table I.

Because of problems in determining contact resistance, and the effect of deviations from hydrostaticity, the results are expressed as resistances rather than resistivities. The isothermal pressure coefficients of resistance are doubtlessly imprecise. However, the relative positions of the isotherms at various pressures were checked from isobaric data. The existence of resistance discontinuities, maxima, etc., should not be affected by the problems discussed above. As discussed in Refs. 1 and 2, the calibration is made with increasing pressure, and pressures can only be determined accurately in this part of the cycle because of permanent deformation of pistons and pyrophyllite. Resistances were also measured with decreasing pressure, and all the features (maxima, minima, discontinuities, etc.) appeared. Except as noted (e.g., barium), the magnitude of these features and degree of sluggishness was the same on decreasing as on increasing pressure. Each isotherm was determined at least five times (some as many as twelve) with different loads and samples.

The purities of the materials were not high by electronic standards, but this probably did not affect the qualitative features; e.g., there was no significant difference in results obtained with reagent grade calcium and with the very high purity material furnished by Dr. F. H. Spedding and Dr. O. N. Carlson of Iowa State University.

## MAGNESIUM

Figure 1 shows the pressure-resistance data for magnesium. At 296°K the resistance initially decreases

TABLE I. Source and purity of materials.

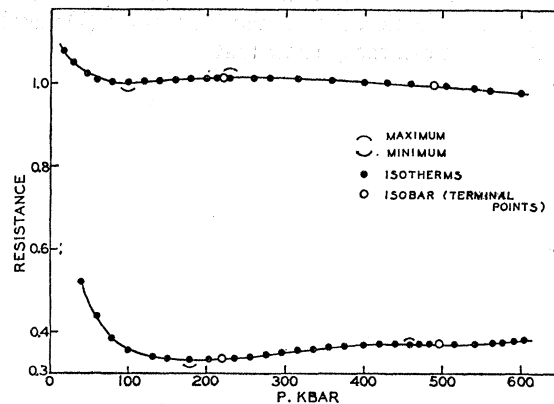| Material | Source | Purity |
|---|---|---|
| Magnesium | Laboratory stock | 99.9+ |
| Calcium | (1) Baker and Adamson | Reagent |
| | (2) Dr. O. N. Carlson Dr. F. H. Spedding | "High purity" |
| Strontium | A. D. Mackay | 99+% |
| Barium | Fisher Chemical Company | 99.9% |

FIG. 1. Resistance versus pressure—magnesium.

with pressure. There follows a minimum in resistance at 80 kbar and a maximum at 230 kbar. At 77°K the first features are repeated, i.e., there is an initial decrease, a minimum at 180 kbar and a maximum at 460 kbar. An additional feature, a final upturning in resistance, is observed at 77°K. At both temperatures the over-all changes in resistance after the initial minima are small (2% at 296°K, 12% at 77°K). The open circles represent terminal points of isobars.

Since magnesium is metallic because of overlapping of bands, the slight variations from "normal" behavior may be due to variations in the degree of overlap with pressure.

## CALCIUM

Earlier measurements of resistance versus pressure for calcium by Bridgman[3] to 65 kbar showed a continuous rise in resistance to the highest pressure he obtained. Our measurements indicate a rather complex and interesting behavior which is difficult to resolve quantitatively because of the sluggishness of the transitions involved.

Below about 70 kbar it is difficult to separate the effects of changing contact resistance from the events characteristic of calcium. Thus, we could not identify the transition noted by Bridgman[4] at 60 kbar. Above this pressure, at 296°K, there is a very small rise in resistance with pressure to about 140 kbar. At this point the resistance increases much more rapidly and drifts upward with time as is characteristic of a sluggish first-order phase transition. The drift dies out in a few moments but reinitiates when a further increment of pressure is applied. By 300 kbar the total rise above 140 kbar is about a factor of 5. At about 300 kbar a new phenomenon appears. On application of pressure the resistance rises initially but then starts to drift *downward*. At higher pressures the downward drift is accelerated, until there is a considerable net decrease in resistance with pressure.

The 77°K isotherm has a qualitatively similar behavior except that the first rise was more sluggish initially, but greater eventually. At 390 kbar the resistance was some 20 times the 140-kbar resistance. Above 390 kbar, the resistance would, on some runs, drop precipitously, while on other runs it would drop off slowly.

In order to establish the temperature coefficient of resistance accurately as a function of pressure, a series of isobars was obtained at 100, 200, 255, 360, 390, and 430 kbar. At each pressure the cell was cooled to 77°K, heated to 296°K, recooled, and so on. The cycle was continued until the terminal values did not change from cycle to cycle. The isotherms shown in Fig. 2 were then constructed, combining isotherms and isobars. The points shown are from isobars.

[3] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **81**, 165 (1952).
[4] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **74**, 425 (1942).
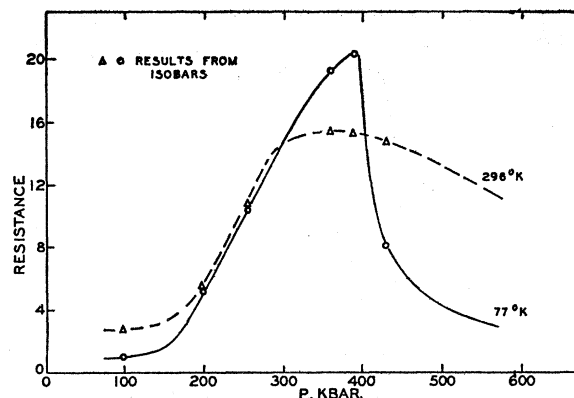
FIG. 2. Resistance versus pressure—calcium.

The results can be summarized as follows: At low pressures calcium has the bcc structure (phase $A$). At 140 kbar a sluggish transition to phase $B$ initiates. At 300 kbar, before the $A$-$B$ transition is complete, a second transition starts ($B$-$C$), and runs, also somewhat sluggishly. There exists also the possibility of the low-pressure transition mentioned by Bridgman.[4]

The calcium atom contains only completely filled atomic orbitals. The solid is metallic because there is an overlap between a filled shell and a neighboring empty shell.

From the isobars it appears that phase $B$ is semimetallic ($R_{77°K}/R_{296°K} = 1.33$ at 390 kbar). The third phase $C$ would seem to be metallic.

## STRONTIUM

Bridgman[3] observed a sharp maximum in the resistance of strontium at about 40 kbar. This maximum was also observed in our studies. Just beyond the maximum there is a sharp drop in resistance accompanied by a drift downward with time, which is typical of a first-order phase transition. There is a maximum also in the 77°K isotherms, which appears to be slightly displaced to higher pressures, although our equipment is not well adapted to studies in this pressure range. Results are
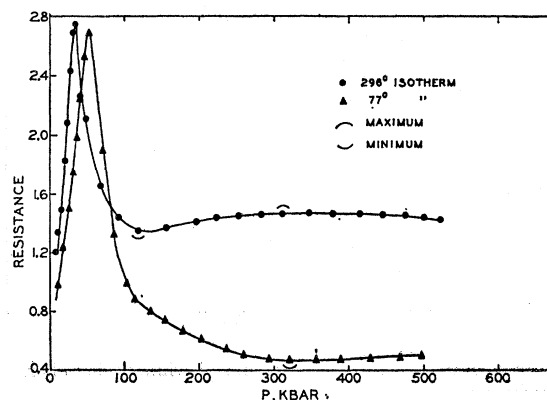


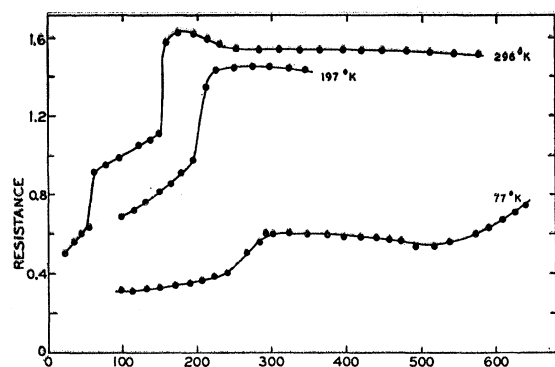FIG. 3. Resistance versus pressure—strontium.

FIG. 4. Resistance versus pressure—barium.



FIG. 6. Phase diagram—barium.

shown in Fig. 3. As far as could be determined from our isobaric measurements, there was substantially zero temperature coefficient of resistance near the maximum. In this pressure range in our apparatus there are small pressure drifts which could have concealed a small gap at the maximum. Such a gap was actually observed with ytterbium.[5] After the phase transition, strontium is definitely metallic. At 296°K there is a minimum at 100 kbar and a broad maximum at about 300 kbar. The 77°K isotherm has a slight minimum at about 320 kbar.

Like all the alkaline earth elements, strontium has filled atomic shells. The solid is, thus, metallic only because of overlap between bands. Apparently the overlap decreases with pressure until, near the maximum, strontium is a semimetal, if not a semiconductor. The transition may involve the promotion of a 4s electron to a band arising from the atomic 3d state, as speculated by Lawson.[6]

## BARIUM

Figure 4 shows the pressure-resistance characteristics of barium at 296, 197, and 77°K. 296°K data have also been reported previously by Balchan and Drickamer.[1] After a low-pressure minimum the resistance rises linearly. There is a sharp rise at 58.5 kbar, a second
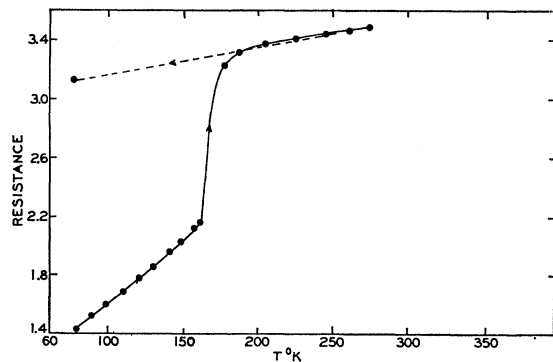


FIG. 5. Resistance versus pressure—barium at 440 kbar.

[5] R. A. Stager and H. G. Drickamer, Science 139, 3561 (1963).
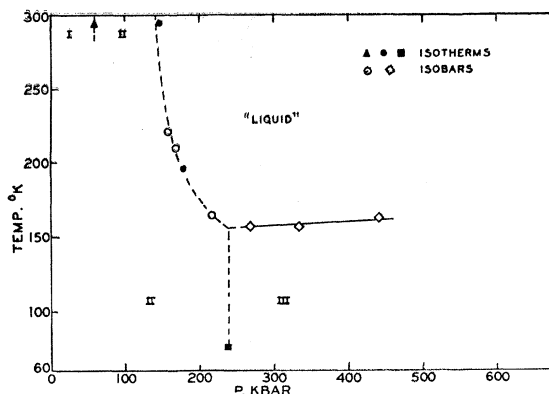[6] A. W. Lawson, Progr. Metal Phys. 6, 1 (1956).

linear region and another sharp rise at 144 kbar. A definite maximum follows.

At 197°K a similar curve is obtained, except that the second rise occurs at 190 kbar. To avoid dragging out the 58.5-kbar transition, for low-temperature isotherms, cooling was done after this transition.

At 77°K, beyond 100 kbar, a gradual rise in resistance with pressure is observed. At 240 kbar a marked break in the curve is observed, after which the rise is much steeper. In striking difference to the two higher temperature isotherms, the high-pressure maximum in resistance appears abruptly, after which an essentially flat region is observed. The resistance breaks downward at 380 kbar to show a minimum at 540 kbar and then an accelerating rise in resistance.

Figure 5 is a typical isobaric run at 440 kbar. The rise from 77 to 160°K is characteristic of a solid metal. The sharp rise at 160°K is quite analogous to the transition observed at 144 kbar and 296°K. (Incidentally, this transition is very sharp with increasing temperature but sluggish with decreasing temperature. This point will be important in the interpretation.) The high-temperature phase shows a small positive-temperature coefficient of resistance. The value is much more typical of liquid metals than of the solid state.

From a series of isotherms and isobars the phase diagram shown in Fig. 6 has been constructed.

The designation of the high-pressure, high-temperature phase as "liquid" must remain tentative until x-ray studies can be obtained. Points in favor of this designation are

(1) Cooling of this phase shows it to be very metastable, as mentioned above; liquids tend to subcool.

(2) Cooling also shows a very small temperature coefficient of resistance for this phase.

(3) Investigation of barium by Kennedy[7] has shown a maximum in the melting point of 1040°K at 15 kbar followed by a continuous lowering of the melting point with pressure as far as data were taken (65 kbar). The

[7] G. C. Kennedy (private communication).

melting point curve of Kennedy could easily join with the II-"liquid" curve in Fig. 6.

If it is indeed liquid, it is interesting to note that barium is then a liquid at temperatures and pressures where even helium should be solid.

The solid II phase is obviously denser than solid I (the transition is probably bcc-fcc). The liquid phase must be denser than solid II. It should be noted, however, that solid III is slightly denser than the liquid. The transition II-III must then take place with a large volume decrease. It may well involve the promotion of an electron from the $6s$ shell to a band arising from the atomic $5d$ state, in analogy to the transition observed in cesium by Bridgman.[3]

# Evidence for Covalent Bonding from Electron Spin Resonance Spectra of Some Rare-Earth Ions in Single Crystals of Calcium Oxide*

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Investigations of electron spin resonance (ESR) spectra of $Yb^{3+}$ and $Dy^{3+}$ in the cubic crystal field of calcium oxide show $g$ factors which are smaller than the calculated $g$ factors. It is shown that covalent bonding through the effect of the orbital reduction factor can explain these discrepancies. It is found that $(1-k)$ is about 0.04, much smaller than found in the iron group, but larger than that found for rare earth ions in the crystal field of $CaF_2$. From the ESR spectra of $Dy^{3+}$ and $Er^{3+}$ it is inferred that the fourth-order potential $B_4$ is at least 200 times larger than the sixth-order potential $B_6$.

RECENT investigations of rare-earth ions in the calcium oxide lattice have been confined to the $S$-state ions, $Eu^{2+}$ and $Gd^{3+}$.[1-4] In both these cases, the spherically symmetrical $S$-state wave functions have given rise to intense cubic spectra, although much weaker noncubic spectra were observed in $Gd^{3+}$.[4] As CaO is the first lattice in which rare earths have been substituted into a site of octahedral symmetry, it is of great interest to extend the investigation to non-$S$-state ions, in which the relative strengths of the crystalline field potentials may be obtained more directly. In this note we discuss the results of experiments on single crystals of CaO containing $Yb^{3+}$, $Dy^{3+}$, and $Er^{3+}$.[5] It will be shown that covalent bonding must be taken into account to explain the experimentally measured $g$ values for $Yb^{3+}$ and $Dy^{3+}$.

## $Yb^{3+}$, $4f^{13}$, $^2F_{7/2}$

This was the simplest system investigated, with an electronic configuration consisting of a single hole in the $4f$ shell. In the pure octahedral field of CaO, the $\Gamma_6$ level, with a theoretical $g$ value of 2.667, should lie lowest for all values of the crystalline field potentials.[6]

At 20°K, an isotropic spectrum was observed with $g = 2.585 \pm 0.003$, $A(171) = (578 \pm 5)$ $G = (698 \pm 6) \times 10^{-4}$ $cm^{-1}$. The measurements were made over the frequency range 8.2 to 11.2 kMc/sec. No significant deviations of the $g$ factor were found in this frequency interval. The linewidth (between points of half-maximum intensity) was approximately 12 G, enabling accurate measurement of the hfs of the odd isotope $^{171}Yb (I = \frac{1}{2})$ only.

A striking feature of these results is the 3% reduction of the experimental $g$ value, when compared with the theoretical value for the $\Gamma_6$ level. This discrepancy provides strong evidence for the existence of covalent bonding in the rare-earth ions. Bleaney[7] has come to a similar conclusion in order to explain the smaller discrepancy in the $g$ value found for the isoelectronic $Tm^{2+}$ in $CaF_2$.[8,9] The experimental values can be explained by introducing the orbital reduction factor. In the case of octahedral symmetry the calculation is relatively simple because there is no admixture from the excited $J = \frac{5}{2}$ level since this level does not contain the $\Gamma_6$ representation. When the factor $k$ is included, the $g$ value of the $\Gamma_6$ level becomes $(7/3)g_J'$, where $g_J'$ (the

[1] W. Low and R. S. Rubins, Phys. Letters 1, 316 (1962).
[2] A. J. Shuskus, Phys. Rev. 127, 1962 (1962).
[3] A. J. Shuskus, Phys. Rev. 127, 2022 (1962).
[4] W. Low and R. S. Rubins, in *Proceedings of the First International Conference on Paramagnetic Resonance* (Academic Press Inc., New York, 1963), p. 79.
[5] The crystals were supplied by Semi-Elements Inc., Saxonburg, Pennsylvania.

[6] K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids 23, 1381 (1962).
[7] B. Bleaney (private communication) and also reported at the Quantum Electronics Conference, Paris, 1963 (unpublished).
[8] W. Hayes and J. W. Twidell, J. Chem. Phys. 35, 1521 (1961).
[9] W. Low and U. Ranon, in *Proceedings of the First International Conference on Paramagnetic Resonance* (Academic Press Inc., New York, 1963).