Pressure-induced superconductivity in strontium and barium

K. J. Dunn and F. P. Bundy
General Electric Company, Corporate Research and Development, Schenectady, New York 12301
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The electrical-resistance behavior of strontium is studied for various pressures from 250 up to 500 kbar and for temperatures from 2 to 300 K. Superconductivity has been observed in strontium for pressures higher than 350 kbar. The superconducting transition temperature varies from 3 to 4 K with dT_c/dP being positive in the pressure range investigated. Superconductivity in Ba is also investigated for pressures from 200 to 400 kbar. dT_c/dP for Ba becomes negative in this pressure range.

I. INTRODUCTION

Strontium is one of the elements in the family of alkaline-earth metals. Since the discoveries of superconductivity in the neighboring elements Sc, Y, La, Ba, and Cs in the periodic table by Wittig and coworkers[1–4] and the recent work on Ca by Dunn and Bundy[5] in which they reported the possibility of Ca becoming superconducting near 2 K at 440 kbar, Sr becomes the next natural candidate for finding superconductivity at high pressures. Previous work[2] indicates Sr is not superconducting for pressures up to 150 kbar and temperatures down to 1.3 K. In this paper, we report the discovery of pressure-induced superconductivity in Sr at pressures from 350 to 500 kbar. The superconducting transition temperature varies from 3 to 4 K for various pressures. dT_c/dP is positive in the pressure range investigated. Superconductivity in Ba is also investigated for pressures from 200 to 400 kbar. dT_c/dP becomes negative in this pressure range. The similarity of the electrical properties in Ca, Sr, and Ba is discussed in light of the experimental findings.

In the early attempts to explain the superconductivity in La, Hamilton and Jensen,[6] and Kondo[7] proposed models involving the presence of $4f$ electrons near the Fermi level. Later, the discovery of the pressure-induced superconductivity in Y by Wittig[2] indicates the presence of $4f$ electrons is not a necessary condition for the occurrence of superconductivity. The appearance of superconductivity and the positive values for dT_c/dP as observed for Y and Ba are then attributed by Wittig[2] to the development of d character in the electron wave functions as suggested by the work of Vasvari *et al.*[8] on the band structure of alkaline-earth metals or to the s-d electronic transition similar to that proposed by Sternheimer[9] in explaining the volume discontinuity for Cs at about 45 kbar. The corresponding rise of the electron-phonon coupling constant may thus cause an increase in T_c to attainable temperatures. The present result of the pressure-induced superconductivity in Sr provides an additional example along this line.

II. EXPERIMENTAL

The pressure equipment used in this investigation is the cryogenic clamp-type sintered-diamond-tipped anvil apparatus. The experimental procedure and pressure calibration have been described elsewhere.[10–12]

The strontium metal of 99% purity was obtained from Ventron Corporation. The samples were prepared under white oil by rolling freshly cut metal chips with a carbide scriber to form thin foils of about 0.07 mm thick. Specimens of rectangular shape of approximately 0.13×0.6 mm^2 were cut and placed in the high-pressure cell as quickly as possible. Figure 1 shows the typical result of the resistance for Sr versus applied pressure at room temperature. The well-known resistance peak near 35 kbar was not observable because of the large initial contact resistance which could be partly due to the thin oxide layer formed on the surface of the specimens. From 100 to 170 kbar, Sr is presumably in bcc phase.[13] At around 170 kbar, there is a definite change of slope in dR/dP. Near 320 kbar, there is another small change in dR/dP. The rise in resistance could be due to a phase transformation or an s-d electronic transition which increases the electron-phonon scattering. An x-ray diffraction study for Sr at high pressure would be most helpful in this connection. Figure 2 shows the R vs T curves for Sr at various fixed cell pressures from 250 up to 500 kbar. No superconductivity was detected for the runs at 250 and 300 kbar down to 2 K. The superconductivity transition observed for pressures above 350 kbar are shown in the insert of Fig. 3. In Fig. 3, we also plot the results of T_c vs P for Sr. The values of T_c and its upper and lower bound as indicated by the error bars are defined as the temperatures at which R/R_n equals 0.5, 0.9, and 0.1, respectively. The uncertainty in pres-

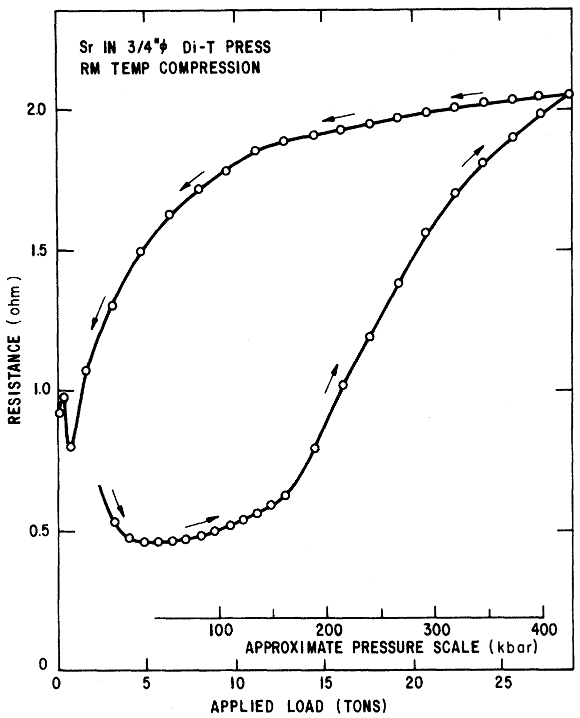

FIG. 1. A typical result of electrical resistance of Sr vs applied pressure at room temperature.

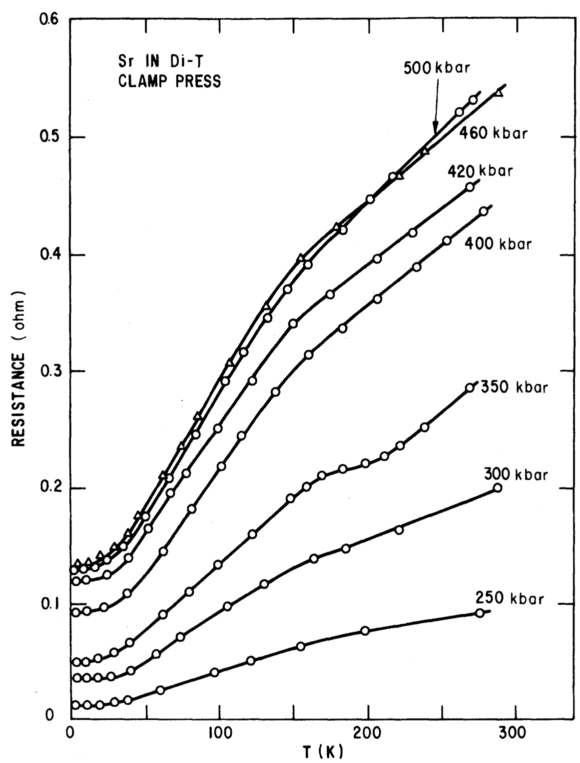

FIG. 2. The resistance vs temperature curves for Sr of various isobaric runs.

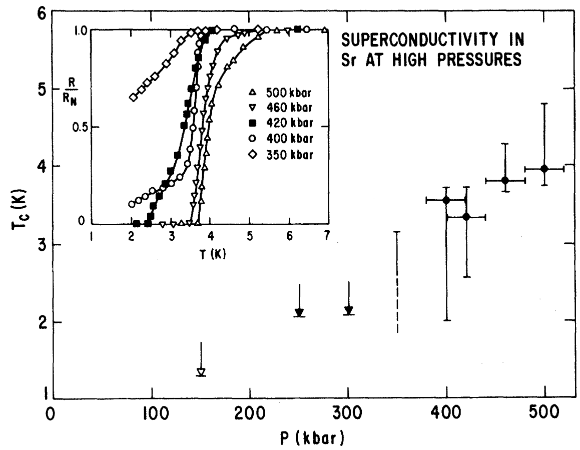

FIG. 3. The superconducting transition temperature T_c for Sr as a function of pressure. The arrow and bar sign represents no superconductivity found at that (P,T) condition. The white-head arrow and bar sign indicates the result of previous work by Wittig (Ref. 2).

sures is estimated to be around 20 kbar. The open-headed arrow and bar sign at 150 kbar and 1.3 K represents the previous work by Wittig[2] in which no superconductivity was found in Sr. The two solid-headed arrow and bar signs at 250 and 300 kbar indicate the present result of no observed superconductivity. dT_c/dP is positive. However, an estimate of its exact value is inappropriate because of the large uncertainties involved.

Among the isobaric runs shown in Fig. 2, there were some nonuniformities in sample size and different degrees of oxidation of sample surface. The comparison between them can be only qualitative rather than quantitative. These curves, however, do provide some useful information. In the 350-kbar run, the kink in R vs T curve around 200 K is most likely an indication of a phase transformation of some sort. The dR/dT in the intermediate temperature range from 50 to 150 K shows a definite increase as the pressure increases from 250 to 500 kbar. This indicates that a major change in the electronic band structure has occurred which results in the changes in the probability of electron-phonon scattering and/or the change in the density of charge carriers.

Superconductivity in Ba has been studied by many research groups[4,14–17] for pressures below 200 kbar. Bastide *et al.*[18] reported a new phase, Ba III, above 85 kbar based on a differential thermal analysis (DTA) investigation at elevated temperatures. Il'ina and Itskevich[14] observed that the superconducting temperature T_c for Ba decreases rapidly from 3 to 1.5 K above 85 kbar within a small pressure range of 10 kbar, supporting the result of Bastide *et al.* However, Moodenbaugh and Wittig[16] found a monotonically increasing T_c for Ba as a function of pressure up to 170 kbar. Whether there is a correlation between T_c and

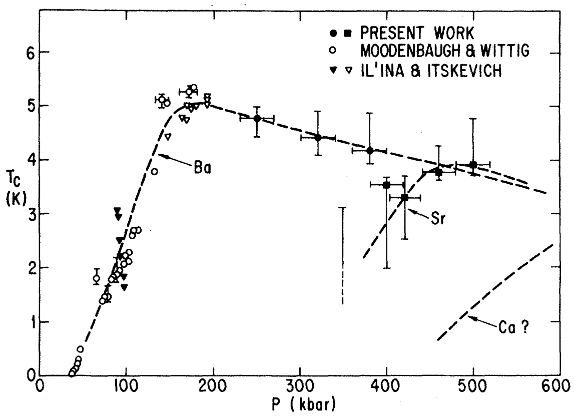

FIG. 4. The T_c vs P curve for Ba, Sr, and Ca. ●, ■ represents data of present work, ○ data of Refs. 4, 16, 17, and ▽, ▼ data of Refs. 14 and 15.

the high-pressure phases of Ba II and Ba III is not clear. We have measured T_c of Ba in the pressure range from 200 to 400 kbar. Our results are shown in Fig. 4 along with those of the previous works. We notice that T_c for Ba increases as the pressure increases until it reaches a maximum around 180 kbar and starts slowly decreasing beyond that. Our results on Sr and Ca are also shown in Fig. 4 to indicate the T_c vs P behavior for Ba, Sr, and Ca in perspective. A question mark is shown for Ca because the superconductivity in Ca is not fully established.[5] Three experiments on Ca were done at the upper pressure capability of our apparatus, one at the second resistance maximum near 420 kbar, and two at pressures higher than that. In the former case, we found the residual resistance remained constant down to the lowest-temperature limit of our apparatus around 2 K. In the latter case, we found at the low-temperature end the residual resistance decreased by 1% in one experiment and 2.5% in the other. If this indeed is the precursor of a superconduction transition, the trend seems to suggest a positive dT_c/dP for Ca. These are, of course, speculative at the present stage.

III. DISCUSSION

There are many similarities in the electrical behavior of Ca, Sr, and Ba. The electronic band structures for these three alkaline-earth metals are very similar to each other as discussed by Vasvari *et al.*[8] Upon application of pressure, the conduction band tends to shift away from the valence band, reducing the Fermi surface and increasing the resistivity. Ca is in fcc structure at zero pressure. Its R vs P curve has a maximum near 180 kbar. Beyond that, Ca probably transforms into a different structure.[5] Sr is also in fcc structure at zero pressure. It transforms into bcc phase around 35 kbar with an associated resistance maximum near the transition. Ba, already in bcc structure at zero pressure, shows superconductivity in the millidegree region around 30 kbar.[17] Judging from Fig. 4 and all these similarities among Ba, Sr, and Ca, it is possible that Sr could become superconducting in the millidegree region around 300 kbar and reach maximum T_c around 500 kbar. Ca probably will behave the same at much higher pressures.

Early work of pseudopotential calculation by Allen and Cohen[19] indicated that the electron-phonon interaction in Ca, Sr, and Ba at zero pressure could be too small to produce superconductivity. According to the band structure work of Vasvari *et al.*,[8] the compression of these elements will result in strong d admixture into the wave functions near the Fermi level. If this assertion is in fact correct, then the appearance of superconductivity under pressure in Ba and Sr suggests that the d-like character of the wave functions at the Fermi level of alkaline-earth metals may play a very important role.

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