[Note that the inequality (6) is correct as it stands for pure Coulomb forces because U_C in (8) is identically zero. If short-range potentials are included there will also be surface terms, as in the cube construction, but these present only a technical complication that can be handled in the same manner as before.[1]] While Eq. (9) is more complicated than (7), it is readily proven explicitly that f_k approaches a limit as $k \to \infty$. [Indeed, it follows from the theory of the renewal equation[9] that (9) will have a limit if $\sum_1^\infty j\varphi_j < \infty$.]

The possibility of packing spheres this way is provided by the following geometrical theorem which plays the key role in our analysis. We state it without proof, but we do so in d dimensions generally and use the following notation: σ_d = volume of a unit d-dimensional sphere $= \frac{4}{3}\pi$ in three dimensions and $\alpha_d = (2^d - 1)2d^{\frac{1}{2}}$.

(T5) Let $p \geqslant \alpha_d + 2^d \sigma_d{}^{-1}$ be a positive integer. For all positive integers j, define radii $r_j = p^{-j}$ and integers $n_j = (p-1)^{j-1} p^{j(d-1)}$. Then it is possible to place simultaneously $\bigcup_j (n_j$ spheres of radius $r_j)$ into a unit d-dimensional sphere so that none of them overlap.

The minimum value of p required by the theorem in three dimensions is 27.

Many of the ideas presented here had their genesis at the Symposium on Exact Results in Statistical Mechanics at Irvine, California, in 1968, and we should like to thank our colleagues for their encouragement and stimulation: M. E. Fisher, R. Griffiths, O. Lanford, M. Mayer, D. Ruelle, and especially A. Lenard.

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SUPERCONDUCTIVITY OF BARIUM UNDER PRESSURE[*]

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Superconductivity of barium is observed under high volume compression. The high-pressure phase, Ba II, has a T_c somewhat lower than 1.3°K at 55 kbar, T_c sharply rising with increase of pressure. A second solid phase above 140 kbar has a T_c of approximately 5°K.

Since the discovery of superconductivity in cerium,[1] barium was also thought to become superconducting under pressure. If there is a common origin of superconductivity in neighboring lanthanum and cerium it seemed worthwhile to look at barium, naively assuming similar electronic properties might exist if it were compressed to the same density.[2] The abnormal pressure dependence of the electrical resistivity[3] (cf. Fig. 1) as well as the highly abnormal P-T phase diagram showing two maxima of the melting temperature[4] indicate fundamental changes of electronic structure with pressure.

The apparatus and procedure have been described in a recent publication.[5] Difficulties of sample preparation and cell loading caused by the chemical reactivity of barium as previously mentioned[5] were overcome by covering the thin (20-μ) metal strip with a film of petrolatum. Two disks of Mylar foil (thickness 6 μ) provide protection

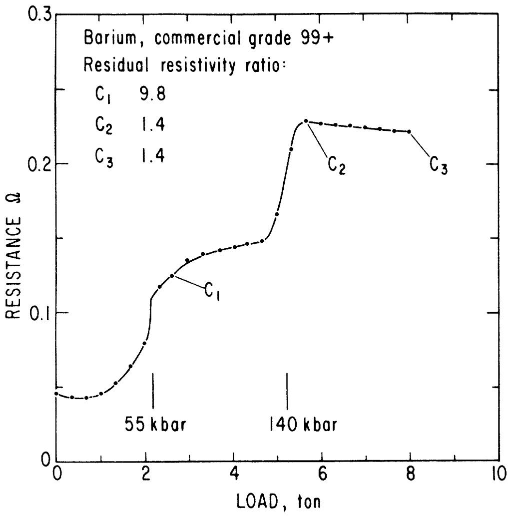

FIG. 1. Room-temperature resistance of barium against press load. The press was cooled to helium temperatures at about 65 (C_1), 140 (C_2), and 170 (C_3) kbar.

against direct contact with the pressure transmitting medium.

Barium from three different sources was used for the experiments. Two samples were of commercial grade and stated to be 99.5% (Mackay) and 99+% (King Laboratories) pure.[6] Both of these samples showed resistivity ratios between 10 and 15. A third sample was cut from a small piece of higher purity Ba.[7] Specimens prepared from this lot had resistivity ratios between 30 and 70 varying from sample to sample and with pressure. All three samples gave essentially the same results so far as the appearance of superconductivity under pressure is concerned. Though we have no analysis on the higher purity material, we conclude from the very consistent picture of all the measurements together that unknown impurities cannot be the reason for pressure-induced superconductivity.

Figure 1 is a plot of the room-temperature resistance of Ba with pressure. Two solid-solid phase transformations at 55 kbar[8] (BaI-II) and about 140 kbar[3] are accompanied by distinct resistance increases. This particular sample was investigated at helium temperatures under pressures of approximately 65, 140, and 170 kbar. The corresponding room-temperature resistance values before cooling are marked $C_1 \cdots C_3$ in Fig. 1. Superconducting transitions were found as shown in Fig. 2 being as high as 5°K at the highest pressure. Samples under a pressure of 55 kbar (just above the BaI-II phase transformation) showed an onset of a normal-to-superconducting transition between 1.5 and 1.3°K, the lowest attainable temperature. Undoubtedly these samples would exhibit full transitions at or below 1°K.

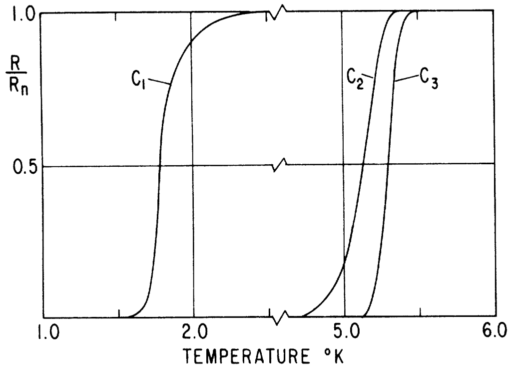

FIG. 2. Superconducting transitions of barium under pressure. $C_1 \cdots C_3$ refer to Fig. 1.

The present apparatus is not ideal for making quantitative measurements of T_c versus pressure between 55 and 75 kbar, but from all the data available there is no doubt that T_c rises sharply with pressure, dT_c/dp being of the order of (1°K)/(10 kbar). This is the cause of the broad transition curves in this pressure range (cf. Fig. 2). One may speculate that the onset of superconductivity in phase BaII and the thermodynamic stability of this phase with pressure are related by the same electronic origin. Very broad transitions were found at pressures between 75 and 140 kbar always shifting to higher temperatures upon increase of pressure. We have at present no explanation for this effect. Another solid phase may appear around 80 kbar as suggested by Bastide, Susse, and Epain.[4] Our resistivity data, however, gave no indication for such an event. After an extremely sluggish phase transformation at 140 kbar,[3] the transition curves became sharper around 5°K (Fig. 2). This transformation has some similarity to the sluggish phase transformations in La. It never ran to completion at room temperature. The residual resistivity ratios of the samples dropped suddenly after this transformation to very low values indicating a two-phase mixture. Thus, we are not quite certain whether the transition temperature found for this phase (Fig. 2) is typical for the pure phase.

There are two possible hypotheses for the occurrence of superconductivity in barium:

(1) At high pressures, there exists a narrow f band very near to or overlapping the Fermi level. One or the other of the f-electron mechanisms

proposed by Kondo[9] and by Hamilton and Jensen[10] for La leads to superconductivity. The sharp rise of T_c with pressure found in La[11] as well as in Ba points towards the same origin of superconductivity.

(2) If the proximity of an f band is irrelevant to the superconductivity of barium, it may be a consequence of the development of d character in the electron wave functions as suggested by the work of Vasvari, Animalu, and Heine[12] on the band structure of alkaline-earth metals or in analogy to Sternheimer's $6s \rightarrow 5d$ electron transfer in cesium.[13] In this case, we would expect cesium also to become superconducting under pressure. Similar arguments should hold for strontium and rubidium. On the other hand, all these three elements also have $4f$ spectroscopic energy levels of similar energy as Ba.[14] An extended investigation for superconductivity under pressure of alkali metals and alkaline earths will be necessary to decide this question.

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EVIDENCE FOR LONG-RANGE EXCITON-IMPURITY INTERACTION IN TETRACENE-DOPED ANTHRACENE CRYSTALS*

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It is shown that diffusion of singlet excitons cannot explain the time dependence of the fluorescence intensity in tetracene-doped anthracene crystals; however, the predictions of a long-range energy-transfer mechanism can be made to agree with experimental results.

The mechanism of energy transfer in organic crystals has been the subject of extensive investigations and in the most recent work on tetracene-doped anthracene crystals and similar systems, energy transfer is attributed to diffusion of singlet excitons.[1] It has generally been concluded that the exciton-impurity interaction is a short-range interaction, and the exciton diffusion coefficient D is on the order of 10^{-3} cm^2 sec^{-1}. In this paper we present experimental data on the time dependence of energy transfer from an anthracene host lattice to tetracene-impurity molecules which cannot be satisfactorily explained by this simple exciton-diffusion theory. The results can be explained by a long-range exciton-impurity interaction, and if the excitons move, the results place an upper limit on the order of 5×10^{-5} cm^2 sec^{-1} on their diffusion coefficient.

Vapor-grown crystals of anthracene doped with 1 and 83 ppm tetracene were investigated.[2] The tetracene concentration was determined from the fluorescence spectra by the method of Kreps, Druin, and Czorny.[3] The samples were excited by a 600-keV x-ray source having a total pulse