PRESSURE-INDUCED SUPERCONDUCTIVITY IN CESIUM AND YTTRIUM*

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Superconductivity has been observed in a high-pressure phase of cesium. Yttrium, normal at zero pressure down to millidegree temperatures, shows pressure-induced superconductivity above 110 kbar, apparently without change in crystal structure. Superconductivity, once restricted to the puzzling case of lanthanum in this part of the periodic system, turns out to be the general phenomenon when we apply pressure.

This Letter introduces two new superconducting elements, cesium and yttrium, which show superconductivity only at high pressure. Previous work had led to the discovery of pressure-induced superconductivity in the cerium[1] and barium.[2] The transition temperature (T_c) of lanthanum increases dramatically up to 12°K at very high pressure ($P = 140$ kbar).[3] A crude extrapolation of the monotonic T_c-P relation to "negative pressures" reveals $T_c \equiv 0$°K for approximately $P = -30$ kbar. Thus the pressure experiments may lead to the notion that the superconductivity of lanthanum at zero pressure is more or less accidental. Adopting this viewpoint, there is now a sequence of three pressure-induced superconducting elements (Ba, La, Ce; cf. Table I) preceding the magnetic rare-earth series.[4]

In the early stage, Hamilton and Jensen[5] suggested that a nonmagnetic virtual bound state, connected with the open $4f$ shell, could cause superconductivity in La. Kondo's two-band model[6] was another attempt to explain the singular behavior of La through a cooperation of f states. With the discovery of pressure-induced superconductivity in lanthanum's left-hand neighbor, barium, we seem to run into difficulties with any model based on $4f$ states at the Fermi surface in promoting superconductivity. Spectroscopic term values of the free Ba atom do not indicate that the f electron collapses into an inner orbit as it does in La.[7] On the other hand, an interesting calculation by Goeppert Mayer,[8] using the Thomas-Fermi approximation, shows that there is an additional attractive trough in the effective potential inside the ion core for an f electron for a couple of elements before the magnetic rare-earths begin. This trough gradually deepens with increasing nuclear charge, finally leading to a bound state. Taking this behavior of an f function into account and postulating that it is reflected in solid-state properties at high pressure, the situation indeed could provide allowance for a virtual bound state in a number of elements preceding the rare earths, if there is one at all. Cesium was studied as the next element in order to investigate the obvious "horizontal" similarity of elements around lanthanum (Table I) with respect to pressure-induced superconductivity.

Table I. Left side of the periodic system featuring the presently known pressure-induced superconductors preceding the classical transition-metal superconductors. The superconducting elements are underlined.

H							
Li	Be						
Na	Mg						
K	Ca	Sc				Ti	V
Rb	Sr	Y				Zr	Nb
Cs	Ba	La	Ce	Pr	•••	Hf	Ta

The apparatus consists essentially of Bridgman anvils, a six-lead resistance cell, and a mechanical press for operation at helium temperatures. It has been described in a previous paper.[9] A dc technique is employed to measure the resistance of the sample and of a strip of lead foil serving as a superconducting manometer. The origin of the high-pressure scale has been reported,[9] along with a discussion of the error limits. Cesium samples were fabricated by filling stainless steel capillaries (25 μ i.d., 75 μ o.d.) with this highly reactive metal. Pieces approximately 1.5 mm in length were cut in a dry box. The cutting process sealed the ends vacuum tight. The characteristic resistance behavior of cesium with pressure[10] was clearly discernible despite the unfavorable ratio of the cross section of the cesium sample in the core and the tubing. Fortunately, the resistivity of the steel proved to be feebly pressure and temperature dependent.

As anticipated, superconductivity was discovered in one of the high-pressure phases of cesium [Cs(V), cf. Fig. 1] which forms after a sluggish phase transformation above ~125 kbar.[11] Figure 1 contains data which were extracted from about 40 measurements on 12 different samples. At very high pressure (~150 kbar), T_c disappears below the temperature limit of the present cryo-

stat (~1.3°K). Arrows indicate that no superconductivity was detected down to that temperature. T_c became measurable in a small "window" around 1.5°K and near 125 kbar due to the metastability of Cs(V) on release of pressure. Considerable pressure hysteresis was introduced by the screening action of the protecting capillary as, for instance, shown by the point with the question mark in Fig. 1, taken on the releasing cycle. We include this point in order to emphasize that the data can only be expected to be qualitatively correct.

It remained to verify that Rb, Sr, and Y in the foregoing row of the periodic table, where certainly no f level will influence solid-state properties, do not show pressure-induced superconductivity. Particularly in view of the precipitous rise of T_c of La with pressure, the study of Y in the same column was considered the crucial experiment. Superconductivity was observed above 110 kbar.[12] Some of our results are displayed in Fig. 2, choosing a straight line to fit the data.

The possibility of a crystallographic phase transformation with pressure can be ruled out on the basis of the following indirect observations. The pressure dependence of resistance is smooth and reversible. The residual resistivity ratio remains virtually constant throughout the whole pressure range ($R_{300°}/R_{4.2°} \approx 10$). A sluggish phase transformation, escaping other detection, is expected to alter this ratio. T_c (cf. Fig. 2) is a reversible function of pressure, regardless of whether the pressure is changed at room temperature or at 1.5°K. The numbers in Fig. 2 denote the sequence of the measurements for two different samples and are primed in those cases in which the pressure was changed at helium temperatures. Evidently, at least above 100 kbar, we study a single-phase sample.

The observation of pressure-induced superconductivity in yttrium clears the mystery about superconductivity in lanthanum.[13] In particular, we note that the "4f electron" is not the necessary condition for the occurrence of superconductivity. We are struck by the high values of T_c found for the whole row, Cs (1.5°K), Ba (5°K), La (12°K), and Ce (1.7°K).[14] Therefore we suspect that there could well be a T_c-enhancing effect in these elements caused by a peculiar shape of the ion-core potential. Experiments with the other alkali and alkaline earth metals will clarify this point.

It has recently been suggested[15] that the superconductivity of La, opposite to all former models, is adversely effected by the presence of a

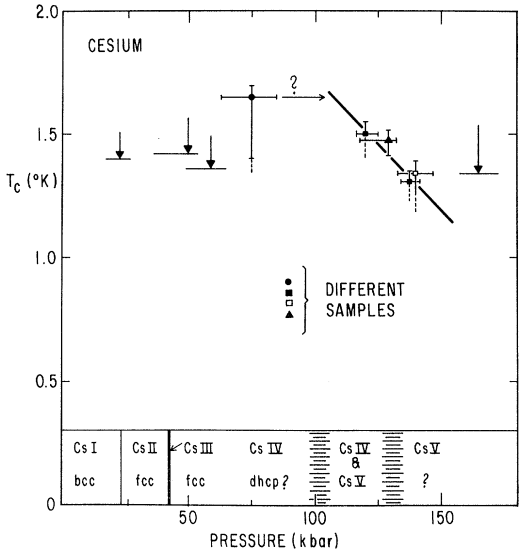

FIG. 1. T_c versus pressure for the phase Cs(V). Arrows indicate the absence of superconductivity. Horizontal bars represent the pressure inhomogeneity along the sample. The inset delineates the regions of stability for the various phases at room temperature.

small amount of localized 4f electrons. Pressure is assumed to raise the 4f level. It is depopulated and therefore T_c increases. This picture does not seem to provide a fruitful approach as it leaves unexplained an "intrinsic" $T_c > 12$°K, higher than any known T_c for pure elements. Barium, on the left side of lanthanum in the periodic system, similarly shows a steep increase of T_c with P, which cannot be explained in this model. Our findings throw doubt on this speculation since they demonstrate that pressure-induced superconductivity is a widespread phenomenon among pretransition metals.[16] Hence we ob-

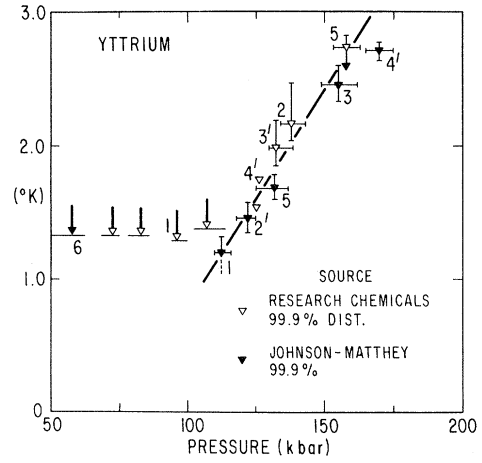

FIG. 2. T_c versus pressure for Y. Error bars are omitted for a few points.

tain, in some cases, positive values for dT_c/dP, as observed for Ba, La, and Y. The origin of this positive sign is definitely not related to f states near the Fermi level, as we learn from the case of Y, and, perhaps, from the positive sign of dT_c/dP for Zr and Ti.[17]

Yttrium is demasked as being "nearly superconducting" at zero pressure; an atomic size effect prevents it from becoming superconducting. According to Fig. 2, it becomes quite likely that we can turn it from a normal metal into a superconductor by a mere change of lattice constant. This experiment, which might require fairly high pressure for pure Y, could also be done with a suitable LaY alloy in order to gain higher precision in the range of nearly hydrostatic pressures. The case of the related isovalent elements Sc and Lu is of particular interest. Looking at the metallic radii, we realize that Lu, with respect to La, is already appreciably "precompressed" by the natural lanthanide contraction at zero pressure. Following this apparently oversimplifying reasoning, one would expect it to show superconductivity at zero pressure, which has not been observed. Maybe it will do so at high pressure?

With respect to cesium, we briefly note that the observation of superconductivity at high pressure substantiates the concept of a pressure-induced "electronic transition" in this metal, for which some evidence existed. The investigation of the other high-pressure phases of cesium (cf. Fig. 1, inset) down to the lowest temperatures is of great interest as they may also show pressure-induced superconductivity. This knowledge will help us to understand the nature of the "electronic transition" which, according to customary notion, is associated with the Cs II-III-IV transformation around 42 kbar.

We try to understand the results in a simple and unifying picture for the whole family of new superconductors (Table I). It seems possible that we are generating "artificial" transition metals under pressure by increasing the d-electron concentration on a particular site.[18] In following Hopfield's[19] description of superconductivity in transition metals, we have to assume that the matrix element, which is usually the "atomic" constant for the center transition metals, strongly increases with compression for the pretransition elements. The corresponding rise of the electron-phonon coupling parameter thus may cause an increase of T_c from very low temperatures to attainable temperatures or may even cause a change in sign for the pairing force when the changes of the Coulomb repulsion are not too strong. It will be of interest to see how T_c depends on P at very low temperatures for Y or Y-based alloys. If the "chemical" approach to the superconductivity of pretransition metals is adequate, we should expect that many alloys and compounds containing the new superconducting elements of Table I will also become superconducting if sufficiently compressed. The study of alloys will, therefore, provide a critical check for this concept.

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[1]J. Wittig, Phys. Rev. Letters 21, 1250 (1968).

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[3]M. B. Maple, J. Wittig, and K. S. Kim, Phys. Rev. Letters 23, 1375 (1969).

[4]In this context the magnetic rare-earth elements begin with Pr as Ce becomes nonmagnetic under pressure (Ref. 3).

[5]D. C. Hamilton and M. A. Jensen, Phys. Rev. Letters 11, 205 (1963).

[6]J. Kondo, Progr. Theoret. Phys. (Kyoto) 29, 1 (1963).

[7]The binding energy of a $4f$ electron in an excited Ba atom is slightly higher than the hydrogen value, but the wave function is essentially outside the core [e. g., D. C. Griffin, K. L. Andrew, and R. D. Cowan, Phys. Rev. 177, 62 (1969)].

[8]M. Goeppert Mayer, Phys. Rev. 60, 184 (1941).

[9]A. Eichler and J. Wittig, Z. Angew. Phys. 25, 319 (1968).

[10]R. A. Stager and H. G. Drickamer, Phys. Rev. Letters 12, 19 (1964).

[11]The authors of Ref. 10 observed the Cs IV-V transformation at ~175 kbar. We comment on this discrepancy and on other details in a comprehensive article.

[12]W. Black investigated the same sample of Y at ambient pressure and found it normal down to 6 mdeg K. In single runs on Rb and Sr, no superconductivity was detected at ~150 kbar. There is considerable doubt as to the purity of the present samples.

[13]Much of the original mystery about the superconductivity of La had been already removed by a study of its thermodynamic properties [D. L. Johnson and D. K. Finnemore, Phys. Rev. 158, 376 (1967)].

[14]T_c of Ba and La are high on an absolute scale. T_c

of Ce (1.7° at 50 kbar) is high in comparison with the tetravalent transition metals Ti, Zr, and Hf. Cs is the first superconducting monovalent metal.

[15]C. F. Ratto, B. Coqblin, and E. Galleani d'Agliano, Solid State Commun. 7, 1387 (1969), and Advan. Phys., to be published.

[16]We call Sc, Y, La, Lu, and Ce pretransition metals also.

[17]N. B. Brandt and N. I. Ginzburg, Zh. Eksperim. i Teor. Fiz. 49, 1706 (1965) [Soviet Phys. JETP 22, 1167 (1966)].

[18]Various experiments have been interpreted along these lines. The idea may have originated from R. M. Sternheimer's calculation [Phys. Rev. 78, 235 (1950)] indicating the possibility of an s-d band crossing for Cs. The statistical model predicts increasing occupation of d states with pressure [P. Gombás, Acta Phys. Hung. 7, 365 (1957); K.-F. Berggren, Phys. Letters 27A, 125 (1968)]. Though rigorous proof is lacking, it seems conceivable that this process happens for pretransition metals at relatively low pressure. The observation that Ce atoms become nonmagnetic under compression (Ref. 3, and M. B. Maple, private communication) supports the idea of a lowering of d-state energy quite well.

[19]J. J. Hopfield, Phys. Rev. 186, 443 (1969).

EFFECT OF FARTHER-NEIGHBOR INTERACTIONS IN MODELS OF SOLID ORTHO-H_2

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If only nearest-neighbor quadrupole-quadrupole couplings are included in a rigid-lattice model of fcc solid ortho-H_2, the usually assumed $Pa3$ order is stable only at the lowest temperatures, and an order with space group $Cmmm$ is stable at higher T. This $Cmmm$ order is destabilized by inclusion in the model of as little as 15% of the unshielded QQ coupling to second and other neighbors. Inclusion of second-neighbor interactions in the model seems necessary and sufficient to eliminate spurious qualitative behavior, and to make appropriate a libron theory starting from the assumption of $Pa3$ order.

The orientational ordering of molecules in solid fcc ortho-H_2 and para-D_2 has been deduced[1,2] from studies of a rigid-lattice model with electrostatic quadrupole-quadrupole orientational coupling between molecules, using the internal field approximation. The predicted structure, with space group $Pa3$ (T_h^6), is one with molecules librating about equilibrium orientations directed along the various threefold axes of the lattice. This structure has been supported by neutron-diffraction studies[3] of solid D_2 containing 83% para-D_2, at 1.9 K. It has been taken as the starting point in development of approximate theories of librational waves in H_2 models with next-neighbor coupling only[4-7], and with interactions between more distant molecules.[8] These theories predict the existence of three Raman-active modes at $\vec{k}=0$, but the observed[9] Raman spectra of ortho-H_2 and para-D_2 (98% pure) at 1.6 K show four components. This and the absence of librational excitations in far-infrared spectra[10] have led Hardy, Silvera, and McTague[9] to suggest that the actual point group may not be $Pa3$, but another with inversion symmetry, such as $R\bar{3}$.

The earlier studies[2] have established the self-consistency of the $Pa3$ structure and its stability near $T=0$ K, where the internal-field method gives internal energies differing only by a factor of 4/25 from those given by the classical theory of interacting quadrupoles.[11] They have not, however, excluded the possibility that another orientational order becomes stable at somewhat higher temperatures. It has therefore seemed desirable to examine this possibility with some care, within the framework of a rigid-lattice model with quadrupole-quadrupole coupling, and in the internal-field approximation.

A method developed[12] in the study of a similar model of hcp ortho-H_2 was found to be a powerful means for identifying orientational orders metastable at low T, but stable at higher T because of their high entropy. These orders were relatively complex, with up to eight molecules per unit cell, and their existence would not have been suggested by symmetry or physical analogy, or by any reasonable amount of intuition. The method involves a division of the molecular lattice into a number of sublattices, with all molecules on a sublattice treated as equivalent. A relaxation procedure using a high-speed computer, starting from an arbitrarily chosen orientational distribution for the molecules on each sublattice, leads to a self-consistent orientational order—an order such that the field derived from the average charge distribution will in turn produce that order. The orders thus found may vary with the assumed tem-