SUPERCONDUCTIVITY INDUCED BY PRESSURE

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It has been known recently that certain metals (Cs, Ba, Y, Ce), located in the lower left corner of the periodic table, reveal superconductivity properties at high pressures but not under ordinary conditions [1, 2]. The reason for this phenomena still remains unclear. In the opinion of [2], the pressure-induced superconductivity in these metals is "due to the form of the potential of the ion."

The purpose of the present paper is to attempt to explain the pressure-induced superconductivity from the point of view of the change of the band structure of the elements under pressure. We shall make use of the results of a numerical calculation of the band structure of different elements as functions of the pressure, details of which can be found in [3]. We also wish to call the experimenters' attention to the fact that superconductivity can apparently occur under pressure also in other metals in the first three groups of the periodic table. In our opinion, the pressure-induced superconductivity can be observed in Rb, Sr, and also in K, Ca, and Sc.

The band structure of metals lying in the first three groups of the periodic table, at weak pressures, is similar in many respects to the energy structure of the free atoms. They are characterized by the presence, besides the s-band, of also d-bands in the first group and partly filled d-bands in the second and third groups. For example, these are the 4s- and 3d-bands in Ca, 5s and 4d in Sr, and 6s and 5d in Ba. With increasing number of the group, the occupation number of the d-bands increases. Ce and other lanthanides differ in that they have a partly filled f-band.

With the increasing pressure, the band structure of these metals undergoes the following significant changes. As the compression is increased, the d-bands that lie above the Fermi surface at normal pressure begin to drop and fall on the Fermi surface. In turn, the s-bands rise and approach the d-bands, so that in some pressure intervals the s- and d-bands overlap. Electronic realignment takes place, such that the electrons go over from the s-bands to the unfilled d-bands. With further compression, the s-band turns out to be unfilled and lies above the d-band.

The pressures at which the electronic realignment takes place depend strongly on the compressibility of the medium and increase with increasing number of the group. In K and Ca, for example, this pressure is 150 - 200 kbar, corresponding to compressions by factors 4 - 5. The table, taken from [3], gives the effective number of the electrons in Ca in different bands, as a function of its degree of compression (δ is the ratio of the density of the compressed medium to the density of the medium at normal pressure). We see that in the case of weak pressure the band filled in the main is 4s, which has 1.9 electrons, while the 3d-band has 0.1 electron (the number of valence electrons in Ca is 2). But at $\delta = 3$ we already have the 3d-band more filled than the 4s-band. At $\delta = 4$, the realignment is completed and all the valence electrons are in the 3d-band.

δ	4s	3d
1,5	1,9	0,1
2	1,5	0,5
3	0,7	1,3
4	0,01	1,99

The electron realignment in other elements is similar, the only difference being that other s- and d- or f-bands take part in it. As to the elements of other groups of the periodic table, particularly the transition elements, with increasing pressure their d-bands also drop, but the electron realignment is less pronounced, since they have sufficiently filled d-bands even at normal pressure.

In this sense the metals K, Rb, Cs, Ca, Sr, Ba, Sc, and Y can be called pre-transitional not only because they lie ahead of the transition element in the periodic table, but because their d-bands become filled with increasing pressure.

Generally speaking, electronic realignment need not necessarily accompany structural phase transitions, but it becomes manifest in many phenomena. For example, in K [4], an anomalous growth of the electric resistivity is observed in the corresponding pressure region. It is characteristic that the dropping of the d-bands becomes noticeable long before the complete overlap of the s- and d-bands. This gives grounds for assuming that the d-levels become resonant with increasing pressure. This fact was recently used as a basis for investigations [5, 6] of the influence of the d-levels on kinetic phenomena in K, Rb, and Cs at normal pressure. The authors of these papers considered the d-levels as resonant ones in the electron-ion scattering and obtain results, particularly for the electric resistivity, which are in better agreement with experiment than the results of others.

Proceeding now to superconductivity, we see that the occurrence of superconductivity under pressure can be easily understood from the point of view of the change in the band structure of the elements. When the pressure is increased, the weakly filled d- or f-levels drop and begin to behave like resonant levels. This affects the electron-ion scattering and leads to an increase in the matrix element of the electron-phonon interaction. The result is the appearance of superconductivity and increase of the electric resistivity with pressure at temperatures above critical.

The possibility that the superconductivity of Ce under pressure is connected with the existence of 4f-levels is discussed in [2], but is regarded as doubtful in connection with the observation of superconductivity in Y, where there is no f-state close to the Fermi surface. From our point of view, these results do not contradict each other, since we assume that the superconductivity of Y is connected with the increase in the number of d-states on the Fermi surface with increasing pressure. We note that transition metals containing 2d-electrons (Ti, Zn, Hf) and more (V, Nb, Ta) are already superconducting at normal pressure, while the temperature of the superconducting transition increases with increasing number of d-electrons.

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