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POSSIBLE EXISTENCE OF A CRITICAL POINT IN FIRST-ORDER ELECTRON TRANSITIONS

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The possibility of a change in electronic states, induced both by a first-order transition and continuously, is established on the basis of qualitative considerations. The critical phenomena associated with the change in the electronic states in a metal and in a metal-dielectric transition are discussed.

IN a number of simple monatomic metals, the spectrum of conduction electrons can be classified by using the concept of electronic states of a system of isolated atoms which is obtained when the lattice spacing of the crystal is increased indefinitely while the structure remains the same. Thus, for example, the conduction electrons in metallic cesium belong to the 6s band, which corresponds to the normal state of the cesium atom. Relatively rough calculations in the Wigner-Seitz scheme[1] show that at sufficiently high densities, the states "originating" from the first excited level 5d of the cesium atom have less energy, and an electron-transition should be observed. In Fig. 1, the broken lines represent the approximate variation of the energy of conduction electrons of cesium per atom for the 6s and 5d levels with the specific volume. The transition in such a scheme should necessarily manifest itself as a first-order transition which occurs when the corresponding values of the chemical potentials are equal. The transition pressure and specific volumes of both phases are determined by the slope and abscissas of the points of tangency of the tangent common to both dotted curves.

To carry the analysis of the qualitative aspect of the problem further, it is convenient to assume that the width of the corresponding bands is sufficiently small; this is justified only in the case of a vanishingly slight interaction between neighbor atoms (strong coupling). At the same time, the energy of the state in the band is independent of the quasimomentum, and it is possible to confine oneself to the consideration of the case where k = 0.

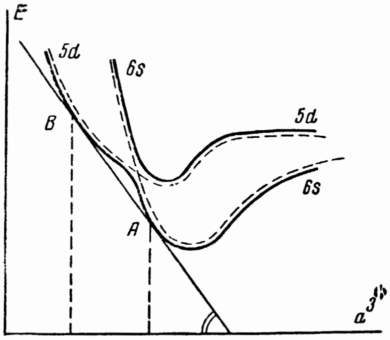

FIG. 1

For each given k, the eigenvalue of the corresponding single-electron Schrödinger equation should be sought in the space-periodic potential as a function of the lattice parameter. For example, for metallic cesium at sufficiently high values of the lattice parameter, the wave function $\Psi_\mathbf{k}$ corresponds to the 6s state. In the region of crossing of the terms, however, the wave function must be taken in the form of the linear combination

$$\Psi_c = c_{6s,\,c}\Psi_{6s,\,c} + c_{5d,\,c}\Psi_{5d,\,c}.$$

At the same time, it is well known that an arbitrarily small disturbance causes the terms not to cross. The variation of the eigenvalues $\epsilon(k)$ of the Hamiltonian with the lattice parameter is qualitatively expressed by solid curves in Fig. 1.

When the finite width of the conduction bands is taken into account, it becomes necessary to consider

$$E = \int^{\varepsilon_F} \varepsilon(\mathbf{k}) \frac{d^3k}{(2\pi\hbar)^3}$$

- the energy of all the states encompassed by the Fermi surface. The picture does not change qualitatively for sufficiently narrow bands. The curve has a segment with a negative curvature where the states are absolutely unstable, and the transition between states A and B remains first-order. However, a broadening of the bands due to electron interaction or to the effect of temperature may distort the lower solid curve so that it will not have the segment with a negative curvature; the electronic transition will then occur smoothly.

A simple analysis shows that the nature of the variation in the thermodynamic quantities fully corresponds to their behavior in the vicinity of the critical point, assuming the absence of an essential singularity at the point itself. Figure 2 shows the change in the chemical potential μ with pressure p in the vicinity of the critical point. As the critical temperature is approached, the size of the loop decreases, and at above-critical temperatures the loop disappears altogether, and the first-order transition is absent.

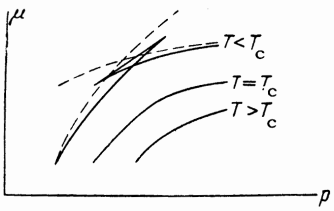

FIG. 2

All of the above considerations pertain of course solely to the case of the so-called "isostructural transitions," when there is a change in the parameter of the lattice without a change in the crystal structure. Actually, a very probable case is one in which, for certain given values of p and T, some new phase of another symmetry has a chemical potential lower than initial, and an isostructural transition cannot take place. It is also evident that the temperature corresponding to the critical point of the isostructural transition should be lower than the melting point of the metal.

The available experimental data on the phase diagram of cesium[2] do not permit one to assert the existence of a critical point for the 6s → 5d transition. Another question which remains open is the 5s → 4d transition in rubidium [1]. It can be stated only that if an electronic transition must occur when the substance is highly compressed, then the effect of broadening of the conduction band, which is proportional to a^{-2} (a is the lattice spacing), becomes prevalent over the energy differences between neighboring bands ($\sim a^{-1}$), and the rearrangement of the electronic states should occur smoothly. Apparently, this situation should exist in the case of the electronic transitions at high compressions calculated by Gandel'man [3] by means of the Wigner-Seitz method.

The most interesting example is the $\gamma - \alpha$ isostructural transition in cerium, in which a decrease in the spacing of the face-centered cubic crystal lattice occurs under pressure. Apparently, one of the 4f electrons passes into the 5d shell [4]. On the basis of an analysis of the pressure dependence of the volume jump associated with the transition, Ponyatovskiĭ [5] postulated the existence of a critical point at p = 17.5 kbar and T = 550°K for this transition. Recent experiments [6] have not contradicted this point of view. It would be very interesting to follow the variation in the structure of cesium during the $\gamma - \alpha$ transition while bypassing the critical point. This transition takes place between fairly narrow bands corresponding to deep shells of the cerium atoms.

In conclusion, let us examine the dielectric-metal transition. As noted earlier [7], at absolute zero temperature this transition should be approximately first-order. This means that the graph of chemical potential vs. pressure at absolute zero has a large loop. As the temperature rises, this loop decreases in size, disappearing at the critical point. The question whether the line of first-order phase transitions continues beyond the critical point in the form of a line of second-order phase transitions remains open.

A similar situation prevails in the special case of an isostructural transition in an isotropic phase, i.e., the vapor-liquid metal case. Above the critical temperature, the metal-dielectric transition occurs with a smooth change in resistance. As was shown by I. M. Lifshitz, the noncoincidence of the critical points of liquid-vapor and metal-dielectric transitions is logically admissible, since the conduction electrons do not necessarily provide all of the binding forces in the condensed state. A possible dependence of the thermodynamic potential on the pressure at a temperature below both critical temperatures is illustrated in Fig. 3.

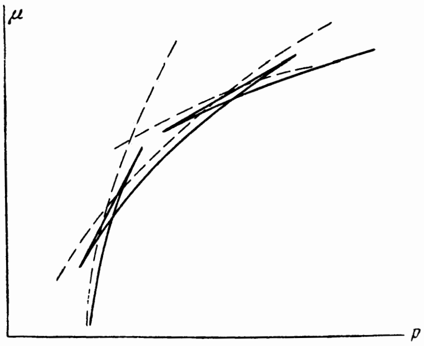

FIG. 3

Recently, Kikoin et al.[8] performed a study of the change in the electrical conductivity of mercury as a function of density under supercritical conditions. This change took place smoothly over more than four orders of magnitude. It is probable that in this specific case of a good metal, in which the majority of the bonding forces are provided by the conduction electrons, there should exist a single critical point both for the liquid-vapor and the metal-dielectric transition.

It is my pleasant obligation to thank Ya. B. Zel'dovich, whose discussion was helpful in elucidating the formulation of the problem. I also wish to thank I. M. Lifshitz and L. V. Vereshchagin for useful comments, and I. K. Kikoin, who communicated the results of his work prior to its publication.

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205