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CONCERNING ISOMORPHIC PHASE TRANSITIONS

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It is shown that an isomorphic phase transition can be realized in metals. Possible T-P diagrams for such a transition are obtained. The critical temperatures and pressure are estimated.

THE change of the topology of the electron Fermi surface under the influence of pressure leads, as indicated by I. Lifshitz[1], to a second-order phase transition without a change of symmetry. It was noted in[1] that at lower pressures an instability of the lattice can arise, leading to a first-order phase transition.

We show in this paper that the change of the Fermi surfaces under pressure (with allowance for the deformation potential) can lead also to a first-order phase transition. As an application, we consider the isomorphic phase transition in cerium.

This problem was considered theoretically by Aptekar and Ponyatovskiĭ [2]. It was assumed that the atoms of metallic cerium are described by discrete levels, and that the two highest levels (4f and 5d) intersect at very low pressure. This is indeed the cause of the phase transition. The theory of[2] is in qualitative agreement with all known experimental facts but one - the large metallic conductivity of cerium. We therefore deem it useful to examine the problem of the isomorphic phase transition from the point of view of the band theory of metals.

We consider a two-band model. We assume that one of the bands is narrow and the other broad (conduction band). We describe both bands in the free-electron approximation with effective masses m_1 and m_2 ($m_1 \gg m_2$). The conditions for the validity of this approximation will be discussed later.

We introduce into the model one more simplifying assumption: the bottom of the narrow band is assumed to be fixed. This assumption is not as arbitrary as appears at first glance. An isolated narrow band with electrons in it should be thermodynamically stable. Consequently, the motion of the center of gravity of the band should be so correlated with the change of the width, that when the crystal is compressed the chemical potential merely increases. The simplest model of this type is a model with a fixed bottom of the band and an effective mass m_1 independent of the cell volume v. The motion of the bottom of the conduction band will be described by the deformation potential.

For a phase transition it is necessary that $d\mu/dv$ be positive in a certain small region of the change of the cell volume. Let us see what happens if the bottom of the conduction band drops when the lattice is compressed. Two effects compete in the change of the chemical potential: an increase proportional to $v^{-2/3}$ and a decrease connected with the lowering of the bottom of the broad band. This is schematically illustrated in Fig. 1. At sufficiently large v (region a on Fig. 1) all the electrons are in the narrow band. Consequently, the chemical potential will increase when the lattice is compressed, owing to the decrease of the density of states in the narrow band. In region b, if the bottom of the conduction band moves sufficiently rapidly, μ can decrease. Finally, in region c the chemical potential will again increase as a result of the strong decrease of the density of the states in the bands.

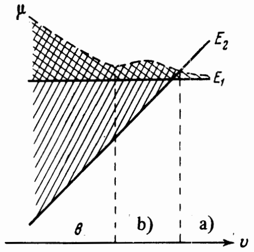

FIG. 1. Qualitative behavior of the chemical potential under hydrostatic compression. E_1 – bottom of narrow band, E_2 – bottom of conduction band, μ – chemical potential.

Actually region a corresponds to large values of v, which can be obtained by stretching the metal (this follows from the subsequent reasoning). Therefore the metal is in region b already at P = 0, corresponding to the band arrangement picture of Fig. 2.

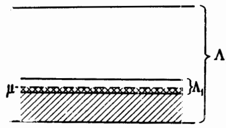

FIG. 2. Arrangement of the bands at P = 0. Λ_1 – narrow band, Λ_2 – conduction band.

It is easy to verify that if the rate of change of the bottom of the conduction band is $dE_2/dv \gg 1/m_2 v^{5/3}$ (we put $\hbar = 1$ throughout), then the region of Δv where $d\mu/dv > 0$ will be of the order of v. This instability will be counteracted by the lattice, which tends to become realigned with change of symmetry. On the other hand, if $dE_2/dv \sim 1/m_1 v^{5/3}$, then $d\mu/dv < 0$ for all v. Consequently, at a certain intermediate value of dE_2/dv there will be a small region of Δv in which $d\mu/dv > 0$.

As is well known, the following conditions should be satisfied for a first-order phase transition:

$$\mu(v_1, T) = \mu(v_2, T), \tag{1}$$

$$P(v_1, T) = P(v_2, T). \tag{2}$$

We are interested here in the jump of the volume δv occurring during the phase transition, the change of the electric conductivity $\delta\sigma$ connected with the change of the number of the conduction electrons in this transition, and also in estimates of the critical temperature and pressure. We determine the pressure with the aid of the thermodynamic relation

$$\left(\frac{\partial\mu}{\partial v}\right)_T=\frac{N_0}{N}v\left(\frac{\partial P}{\partial v}\right)_T, \tag{3}$$

where N is the number of electrons and N_0 the number of cells.

Equation (3) can be rewritten in the form

$$P(v,T)=P(v_0,T)+\frac{N}{N_0}\int_{v_0}^{v}\frac{1}{v}\left(\frac{\partial\mu}{\partial v}\right)_T dv. \tag{4}$$

In a first-order phase transition, there arises a region of metastability Δv, in which $d\mu/dv < 0$. We define v_0 by the equation $d^2\mu/dv^2\,|_{v=v_0} = 0$. We expand $\mu(v, T)$ near $v = v_0$ in powers of $v - v_0$. It is convenient to introduce the symbol $v = v_0x$. Then

$$\mu(x,T)=\mu(1,T)+(x-1)\mu'+{}^1/_6(x-1)^3\mu''', \tag{5}$$

where the prime denotes differentiation with respect to x at constant T and x = 1.

Obviously, small $\Delta v/v$ correspond to $\mu' \ll |\mu'''|$. Using (4) we obtain

$$P(x,T)=P(1,T)+\frac{N}{N_0}\frac{1}{v_0}\Big\{(x-1)\mu'-\frac{1}{2}(x-1)^2\mu' + \frac{1}{6}(x-1)^3\mu'''\Big\}. \tag{6}$$

From (1) and (2) we get

$$x_1-1=1-x_2,\qquad \mu'+\frac{1}{6}\mu'''(x_1-1)^2=0.$$

Consequently,

$$\delta x=x_1-x_2=\frac{\delta v}{v_0}=2\left(-6\frac{\mu'}{\mu'''}\right)^{1/2}. \tag{7}$$

We consider first the case T = 0 and determine the chemical potential as a function of v. Using Fermi statistics for the two-band problem, we obtain $\mu(v, T)$.

We introduce the symbols E_i, g_i, and m_i for the energy of the bottom of the band, the degeneracy multiplicity, and the effective mass. For the narrow band i = 1, and for the conduction band i = 2; ζ_i is the chemical potential reckoned from the bottom of the corresponding band. The position of the bottom of the conduction band is best reckoned from the bottom of the narrow band. We define $\varphi(v)$ by the equation

$$E_2=E_1-\varphi(v).$$

The law of electron-number conservation

$$\sum_{i=1}^{2}(2m_i)^{3/2}g_i\zeta_i^{3/2}=6\pi^2\frac{N}{N_0}\frac{1}{v}, \tag{8}$$

and the equation defining the motion of the bottom of the band

$$\zeta_2-\zeta_1=\varphi(v), \tag{9}$$

enable us to find the chemical potential as a function of the volume. In the first approximation in m_2/m_1 we get

$$\zeta_1(x)=\left(6\pi^2\frac{N}{N_0}\right)^{3/2}\frac{1}{g_1{}^{2/3}2m_1v_0{}^{2/3}}\left[\frac{1}{x}-\psi^{3/2}(x)\right]^{2/3}, \tag{10}$$

$$\zeta_2(x)=\left(6\pi^2\frac{N}{N_0}\right)^{2/3}\frac{1}{g_2{}^{2/3}2m_2v_0{}^{2/3}}\psi(x). \tag{11}$$

Here $\psi(x)$ is connected with $\varphi(v)$ by the formula

$$\varphi(v)=\left(6\pi^2\frac{N}{N_0}\right)^{2/3}\frac{1}{g_2{}^{2/3}2m_2v_0{}^{2/3}}\psi(x) \tag{12}$$

and has a simple meaning, namely:

$$x\psi^{3/2}(x)=N_2/N. \tag{13}$$

The quantity $\varphi(v)$ is of the order of the usual electron energy. Consequently, $\psi(x) \sim 1$. This means that the transition occurs at $N_2 \sim N_1$, in accord with Fig. 2. Obviously, the jump of the volume cannot be large. Therefore, down to P = 0 the metal is not in the region of states a (Fig. 1) and does not experience a second-order phase transition. An increase of the pressure can lead in principle to such a transition (when all the electrons move to the conduction band).

We shall regard the jump of the volume as a small quantity. Indeed, as stated above, realignments of the lattice with change of symmetry compete with large changes of the volume. A small value of the parameter $\Delta v/v = \Delta x$ denotes that near x = 1 the value of μ is proportional to $(\Delta x)^2$ (see Eq. (7)). Putting approximately $\mu' = 0$, we obtain two equations that should be satisfied at the transition point:

$$\psi'=-{}^2/_3\psi^{-1/2}(1), \tag{14}$$

$$\psi''={}^4/_3\psi^{-1/2}(1)-{}^2/_9\psi^{-2}(1). \tag{15}$$

Equation (15) has no independent meaning. It simply determines the choice of v_0 ($\mu'' = 0$). Equation (14) relates the rate of motion of the bottom of the conduction band with the number of electrons in this band. It should be satisfied accurate to $(\Delta v/v)^2$. Such a situation is accidental in the case of pure metals and apparently explains why isomorphic phase transitions have been observed so far only in cerium and in cesium.

We note that equation (14) can be rewritten in the form

$$\frac{1}{N}\frac{dN_1}{dx}=\frac{N_1}{N}. \tag{14$'$}$$

We now consider $T \neq 0$. The equation for the chemical potential is then written in the form

$$6\pi^2\frac{N}{N_0}\frac{1}{v}=\sum_{i=1}^{2}\frac{3}{2}g_i(2m_i)^{3/2}\cdot \times\int_0^\infty\left[\exp\left(\frac{\varepsilon-\zeta_i(x,T)}{T}\right)+1\right]^{-1}\varepsilon^{1/2}\,d\varepsilon. \tag{16}$$

At sufficiently small T ($T^2/\zeta_i^2(x, 0) \ll 1$), as is well known[3], it is possible to carry out an expansion in powers of T; this yields

$$\zeta_1(x,T)=\zeta_1(x,0)-\frac{\pi^2}{12}\frac{T^2}{\zeta_1(x,0)} + \frac{\pi^2}{12}\frac{g_2}{g_1}\left(\frac{m_2}{m_1}\right)^{3/2}\frac{T^2}{\zeta_1^{3/2}(x,0)}\zeta_2^{1/2}(x,0). \tag{17}$$

Near x = 1 we can put

$$\zeta_1(x,0)=\zeta_1(1,0)\left[1+\alpha(x-1)-{}^1/_6C(x-1)^3\right],$$

where $C \sim 1$ and, as seen from (7), $\alpha \sim (\Delta v/v)^2 \ll 1$.

As is well known, the critical temperature T_c is determined from the equations

$$\left(\frac{\partial\zeta_1(x,T)}{\partial x}\right)_T = 0, \quad \left(\frac{\partial^2\zeta_1(x,T)}{\partial x^2}\right)_T = 0. \tag{18}$$

From (17) and (18) we obtain $T_c \sim \zeta_1(m_1\alpha/m_2)^{1/2}$. Since $(\partial\zeta_1/\partial x)_T = \alpha - \beta T^2$, the jump of the volume in the phase transition is $\delta x \sim (\alpha - \beta T^2)^{1/2}$.

Let us consider the possible equilibrium phase diagrams in the P-T plane. In principle, at $T = 0$ two situations are possible, shown in Figs. 3a and 3b. In the former case, when $T = 0$ and $P \geq 0$ there is no phase transition. The transition corresponds formally to a negative pressure (see Fig. 4a). In the second case, the transition takes place at $T = 0$ and $P > 0$, and the phase diagram has the form shown in Fig. 4b.

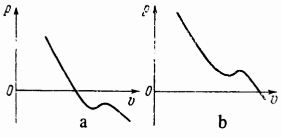

FIG. 3

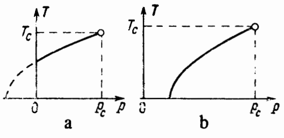

FIG. 4

FIG. 3. P-v diagram at T = 0.

FIG. 4. Possible P-T diagrams of isomorphic phase transition.

Let us estimate the value of P_c. As is well known, the small correction to the thermodynamic potential $\Phi = N\mu$ coincides with the correction to the free energy F, so that

$$\delta F = F(x,T) - F(x,0) = N(\zeta_1(x,T) - \zeta_1(x,0)). \tag{19}$$

The correction to ζ_1 is given by formula (17). We can now readily find the equation of state, which takes the form

$$P(x,T) = P(x,0) + \frac{k}{v_0}\frac{T^2}{\zeta_1(x,0)}\frac{m_2}{m_1}, \tag{20}$$

where k is a factor on the order of unity. In the derivation of (20) we have put $\alpha \ll m_2/m_1$. From (20) it is obvious that

$$P_c \sim \frac{T_c^2}{v_0\zeta_1}\frac{m_2}{m_1} \sim P_0\frac{m_2}{m_1}\alpha,$$

where $P_0 \sim \zeta_2/v_0$ is the characteristic electronic pressure. We note that T_c and P_c turn out to be small compared with the characteristic electronic quantities.

This raises the question why the point $x = 1$ does not correspond to a very large pressure of the order of P_0. The answer lies in the fact that at $P = 0$ the quantity $|1 - x|$ is small. On the other hand, it is seen from (6) that the pressure difference is a small quantity of higher order than $|1 - x|$.

It is of interest to calculate the jump of the electric conductivity σ. The electric conductivity is due to the electrons of the conduction band. The calculation is carried out with the aid of the elementary formula

$$\sigma = n_2e^2\tau_2 / m_2.$$

Using (13) and (14), we get from this formula

$$\frac{\delta\sigma}{\sigma} = -\psi^{-3/2}(1)\delta x = -\frac{N}{N_2}\delta x. \tag{21}$$

The dependence of $\delta\sigma/\sigma$ on T is determined by the temperature dependence of δx.

The phase transition described above is possibly realized in cerium. Judging from the atomic spectra, a narrow 4f band and a broad 5d (6s) band should compete in metallic cerium. An isomorphic phase transition was observed in this metal[4], with a volume jump $\delta x \sim 10\%$. The T-P diagram was obtained[5] as well as the volume jumps δx in some of its points. Interpolating δx to zero, Ponyatovskiĭ[5] found the critical point $T_c \sim 600°K$, $P_c \sim 20$ kbar. The experimental T-P diagram corresponds to Fig. 4a. The transition is accompanied by a jump of the electric conductivity $\delta\sigma/\sigma \sim 20\%$[6], which agrees well with formula (21).

All the foregoing, strictly speaking, is justified in the case when the average number of electrons per atom in the narrow band is much smaller than unity. In the opposite case it is necessary to take into account the localized states. Then the spectrum of the elementary excitations is determined essentially by the Hund energy (see, e.g.,[7]). Therefore the present calculation cannot claim to offer an explanation of the paramagnetic properties of the metal in the isomorphic transition.

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