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INFLUENCE OF IMPURITIES ON AN ISOMORPHIC PHASE TRANSITION

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It is well known that, in a model of a metal with overlapping conduction band and narrow band, an isomorphic phase transition accompanied by a jump of the volume is possible. In this article the influence of substitutional impurities on a transition of this kind is considered. It is shown that impurities lead to an appreciable displacement of the phase transition diagram.

EARLIER[1] it was shown that, in a model of a metal with overlapping conduction band and narrow band, an isomorphic phase transition accompanied by a jump Δv of the volume is possible without a change of the lattice symmetry. Here we shall be interested in the influence of impurities on a phase transition of this type.

First let us consider charged substitutional impurities. For Ce, for example, such impurities are Pr, Nd, and so forth (donors), and Er, Tm (acceptors). We shall assume that the ionic radius of an impurity differs slightly from the radius of an ion of the pure substance. Then the extra electrons (in the case of donors) will fill the unoccupied states in the bands. And conversely, in the case of acceptors the impurities will take electrons which are close to the Fermi surface away from the bands.

Let us briefly call to mind the phase transition mechanism which we considered. For a phase transition of the first kind the following standard conditions must be fulfilled:

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

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

(μ denotes the chemical potential, P is the pressure, and v is the cell volume). In other words, in a certain small region of the change of the cell volume the derivative $d\mu/dv$ must be positive. This condition is fulfilled if the bottom of the conduction band drops when the lattice is compressed. In this connection two effects compete in the change of the chemical potential: an increase proportional to $v^{-2/3}$, and a decrease associated with the lowering of the bottom of the conduction band. If the bands overlap as shown in Fig. 1, where $N_1 \sim N_2$, then at $T = 0$ the chemical potentials (ζ_i) reckoned from the bottoms of the corresponding bands are given by

$$\zeta_1(x) = \left(6\pi^2 \frac{N}{N_0}\right)^{2/3} \frac{1}{g_1^{2/3} 2m_1 v_0^{2/3}} \left[\frac{1}{x} - \psi^{3/2}(x)\right]^{2/3}, \tag{3}$$

$$\zeta_2(x) = \left(6\pi^2 \frac{N}{N_0}\right)^{2/3} \frac{1}{g_2^{2/3} 2m_2 v_0^{2/3}} \psi(x). \tag{4}$$

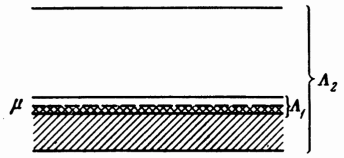

FIG. 1. Arrangement of the bands at P = 0. Λ_1 – narrow band, Λ_2 – conduction band.

Here g_i, m_i, and N_i denote the degeneracy multiplicity, the effective mass of the electrons, and the number of electrons in the corresponding band (for the narrow band $i = 1$, and for the conduction band $i = 2$), N is the total number of electrons, and N_0 is the number of cells in the crystal. The variable x is equal to v/v_0 where v_0 is determined by the equation $d^2\mu/dv^2|_{v=v_0} = 0$. The value of $\psi(x)$ is found from the relation

$$E_1 - E_2 = \left(6\pi^2 \frac{N}{N_0}\right)^{2/3} \frac{1}{g_2^{2/3} 2m_2 v_0^{2/3}} \psi(x) \tag{5}$$

(E_i is the bottom of the appropriate band) and has a simple meaning, namely

$$x\psi^{3/2}(x) = N_2 / N. \tag{6}$$

We assume that E_1 does not change when the lattice is compressed. Therefore, instead of (1) we shall have

$$\zeta_1(v_1, T) = \zeta_2(v_2, T). \tag{7}$$

In order for a phase transition to occur in the neighborhood of $v = v_0$, it is necessary that the following conditions be fulfilled correct to terms of order $(\Delta v/v)^2$:

$$\psi' = -{}^2/_3\psi^{-1/2}(1), \tag{8}$$

$$\psi'' = {}^4/_3\psi^{-1/2}(1) - {}^2/_9\psi^{-2}(1). \tag{9}$$

Expanding (3) near $x = 1$, we obtain the result that for $T = 0$

$$\zeta_1(x) = \zeta_1(x=1)[1 + \alpha(x-1) - {}^1/_6 C(x-1)^3], \tag{10}$$

where $C \sim 1$ and $\alpha \sim (\Delta v/v)^2 \ll 1$.

Let us see how the chemical potential ζ_1 behaves in its dependence on the number of charged impurities ΔN. It is necessary for us to find $\zeta_1(N + Z\Delta N, x)$ (Z is the charge of an impurity). In order to do this, in Eq. (3) it is necessary to make the substitution $N \rightarrow N + Z\Delta N$. The dependence of $\psi(x)$ on N as given by Eq. (6) turns out to be very essential. The density of states in the broad band is much smaller than the density of states in the narrow band; therefore the number of electrons in the conduction band almost doesn't change during the addition of the charged impurities. Hence

$$\psi^{3/2}(N + Z\Delta N, x)(N + Z\Delta N) = \psi^{3/2}(N, x)N. \tag{11}$$

Having substituted (11) into the formula for $\zeta_1(N + Z\Delta N, x)$, we obtain

$$\alpha \rightarrow \alpha - {}^2/_3 Z\Delta N / N_1. \tag{12}$$

Consequently Δv and also the jumps of all the quantities associated with Δv (for example, the jump of the electric conductivity) become of the order of $[\alpha - (2/3)Z(\Delta N/N_1)]^{1/2}$. The critical temperature of a phase transition of the first kind in a pure substance is proportional to $\alpha^{1/2}$. Therefore, a relation exists between the critical temperature $(T_c(\Delta N))$ in the presence of impurities and the critical temperature (T_c) of the pure substance:

$$\frac{T_c(\Delta N)}{T_c}=\left(\frac{\alpha-{}^2/_3 Z\Delta N/N_1}{\alpha}\right)^{1/2}. \tag{13}$$

In addition

$$\frac{P_c(\Delta N)-P_0(\Delta N)}{P_c-P_0}=\frac{\alpha-{}^2/_3 Z\Delta N/N_1}{\alpha} \tag{14}$$

(P_0 is the pressure corresponding to the phase transition at $T = 0$).

Let us find the change $P_0(\Delta N)$. In order to do this it is necessary to differentiate the small correction to the free energy F with respect to V. As is well known, the small corrections to F and to the thermodynamic potential Φ, expressed in the corresponding variables, are equal. The correction to Φ is determined from

$$\Delta\Phi=(N+Z\Delta N)\zeta_1(N+Z\Delta N,\ x)-N\zeta_1(N,\ x). \tag{15}$$

Taking (11) into account, from formula (15) we obtain

$$\frac{P_0(\Delta N)-P_0}{P_c-P_0}={}^2/_3 Z\frac{\Delta N}{N_1}\frac{1}{\alpha}. \tag{16}$$

The dashed curves in Figs. 2 and 3 show the possible $P - T$ diagrams in the case of impurities (curve 1 corresponds to donors, curve 2 corresponds to acceptors).

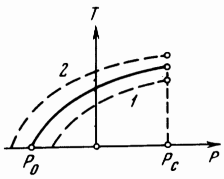

FIG. 2

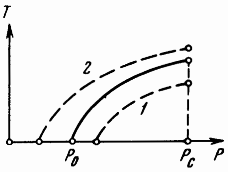

FIG. 3

FIG. 2. P - T diagram of an isomorphic phase transition ($P_0 < 0$).
FIG. 3. P - T diagram of an isomorphic phase transition ($P_0 > 0$).

From Eqs. (14) and (16) we find $P_c(\Delta N) = P_c$ to the approximation under consideration, i.e., the critical pressure does not change. From Fig. 2 it is seen that the addition of donors may lead to the appearance of a phase transition already at $T = 0$. This happens if

$$\Delta N\geqslant\frac{3}{2}\alpha\frac{N_1}{Z}\frac{|P_0|}{P_c-P_0}. \tag{17}$$

The addition of acceptors raises the critical temperature of the phase transition. Therefore, for a sufficiently high concentration of impurities, the $P - T$ diagram may end on the melting curve.

Up to now we have considered charged impurities. Now let us estimate the influence of neutral substitutional impurities. The change of the volume per unit cell is given by

$$\frac{\Delta v}{v}=\frac{\Delta N}{N_0}\frac{\Delta r_{\text{ion}}}{r_{\text{ion}}}$$

(Δr_{ion} is the difference between the ionic radii of the impurity and of the pure substance). Depending on the sign of $\Delta v/v$ the $P - v$ diagram at $T = 0$ rises ($\Delta v/v > 0$) or drops down ($\Delta v/v < 0$). This leads to the result that the $P - T$ diagram of the phase transition is displaced in parallel with the P axis without a change of the critical temperature. Estimates lead to such results as

$$\frac{P_0(\Delta N)-P_0}{P_c-P_0}\sim\frac{\Delta N}{N_0}\frac{\Delta r_{\text{ion}}}{r_{\text{ion}}}\frac{1}{\alpha^{1/3}}, \tag{18}$$

if $|P_0| \sim P_c$, and

$$\frac{P_0(\Delta N)-P_0}{P_c-P_0}\sim\frac{\Delta N}{N_0}\frac{\Delta r_{\text{ion}}}{r_{\text{ion}}}, \tag{18'}$$

if $|P_0| \ll P_c$. From a comparison of Eqs. (18), (18′), and (16) it is clear that the influence of neutral impurities on an isomorphic phase transition is weaker than the influence of charged impurities.

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[1] V. L. Pokrovskiĭ and G. V. Uĭmin, Zh. Eksp. Teor. Fiz. 55, 1555 (1968) [Sov. Phys.-JETP 28, 814 (1969)].

Translated by H. H. Nickle
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