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Effective-medium method, percolation theory and conductivity data applied to study polymorphic transformations in solids under high pressure

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Abstract

An approximate model is proposed for calculating the relative volume phase fractions in the critical region of polymorphic transformations in solids. The threshold values of the effective conductivity and the corresponding pressure P_c, at which an infinite domain of the high-conductivity phase is formed, are determined. It is proposed to define the pressure P_c as the phase transition pressure.

1. Introduction

It is known that the pressure range in which structural phase transformations occur in solids (up to 10 GPa wide, according to x-ray data) coincides with the interval of a stepwise change in the electrical resistance (figure 1) [1–4].

The thermodynamic aspect of the mechanism of phase transformations in solids, which occur, in particular, in isothermal conditions under uniform pressure, was described in [5–8]. Phase transformations in solids proceed in such a manner that, first, a new phase nucleates in the initial phase, because of temperature and pressure fluctuations and presence of defects; and then the appearing nuclei grow, interact and form a complex heterophase system. Under fixed thermodynamic conditions, a certain degree of transformation is reached quite rapidly and remains constant for an arbitrarily long period of time. The relative amount of the new phase is a function of the thermodynamic conditions of transformation. Thus, a two-phase metastable equilibrium of the phases constituting the system is attained in solids in the critical region. We propose to use a modified effective-medium method [9] and the percolation theory to describe mathematically the phase transition from insulator (low-conductivity phase I) to metal (high-conductivity phase II) (the terms 'insulator' and 'metal' are conditional) on the basis of electrical resistance data.

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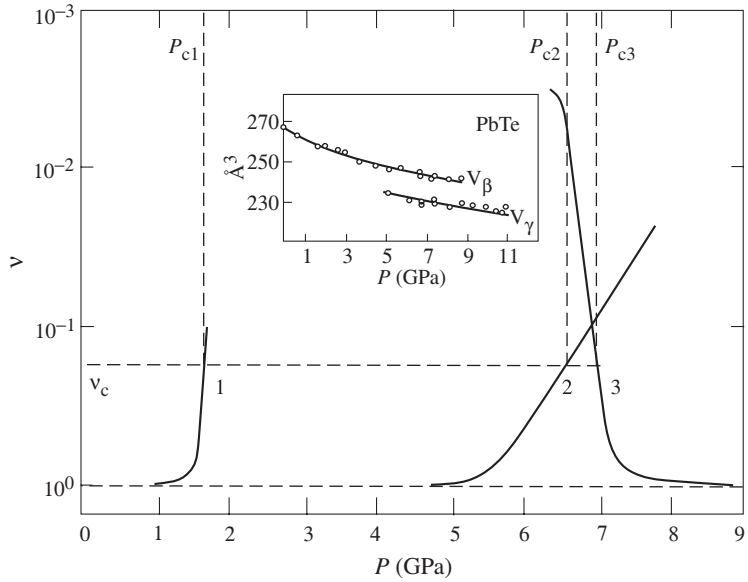

Figure 1. Pressure dependences of the relative volume fractions of phases in n-HgTe [2] (curve 1), p-PbTe [3] (curve 2) and n-InAs [4] (curve 3). P_{c1}, P_{c2} and P_{c3} are the threshold pressures for $\nu_c = 0.17$. Inset: pressure dependences of the unit cell volumes V_β and V_γ of, respectively, the initial and final phases, in PbTe [1].

2. Model of heterophase structure as an effective medium (HSEM)

Let us proceed from the known expressions for resistivity in the effective-medium approximation, used to describe a pressure-induced structural phase transition in a solid under isothermal conditions [9] and a superconducting transition [10]:

$$\rho_{\text{eff}} = \frac{\sum_i \rho_i \nu_i f_i}{\sum_i \nu_i f_i} \qquad f_i = \frac{3\rho_{\text{eff}}}{A_i \rho_{\text{eff}} + (3 - A_i)\rho_i}. \tag{1}$$

Here, i is the phase number, A_i are coefficients taking into account the configuration of phase inclusions, ν_i and ρ_i are the corresponding relative volume fractions and resistivities. For A_i equal to 0, 3 and 1, the phase configuration is filamentary, laminar and spherical, respectively. It is assumed that the coefficients A_i are different for different phases and depend on the degree of transformation, whether the perturbation is isotropic (uniform pressure, isothermal conditions), whether the phase transformation in a crystal occurs without loss of uniformity or plastic deformation of the crystal lattice and whether the sample is macroscopically uniform.

In the I $\rightleftarrows$ II phase transformations, the spherical approximation is adequate at the initial instant of time for the nuclei of phases II (I $\rightarrow$ II) and I (II $\rightarrow$ I), with $A_{\text{II}} = 1$ (I $\rightarrow$ II) and $A_{\text{I}} = 1$ (II $\rightarrow$ I). It is also apparent that insulating layers perpendicular to the electric field and conducting channels parallel to it are formed at, respectively, $A_{\text{I}} = 3$ (I $\rightarrow$ II) and $A_{\text{II}} = 0$ (II $\rightarrow$ I). Thus, we have $A_{\text{I}} = 3$, $A_{\text{II}} = 1$ for I $\rightarrow$ II and $A_{\text{I}} = 1$, $A_{\text{II}} = 0$ for II $\rightarrow$ I at the boundaries of the transition domains. A linear approximation is used for coefficients A_{I} and A_{II} between the boundary values; this approximation is modified by introducing a fitting parameter n for coefficient A_{II}.

Thus, taking the above into account, we have for $0 \leqslant \alpha \leqslant 1$:

$$A_{\text{I}} = 1 + 2(1 - \alpha)(1 - \nu) \qquad A_{\text{II}} = \alpha + (1 - \alpha)(1 - \nu)^n \tag{2}$$

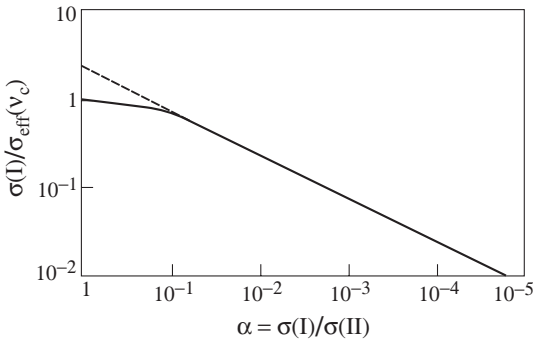

Figure 2. Dependence of $\sigma(\mathrm{I})/\sigma_{\mathrm{eff}}(\nu_c)$ on α for $\nu_c = 0.17$.

where $\alpha = \sigma(\mathrm{I})/\sigma(\mathrm{II})$, $\sigma(\mathrm{I})$ and $\sigma(\mathrm{II})$ are the conductivities of phases I and II and ν is the relative volume fraction of the high-conductivity phase II.

Using relations (1) and (2), we obtain the following equation:

$$kx^2 + Bx + (k-3)\alpha = 0$$

where

$$k = (1-\alpha)[(1-\nu)^{n+1} - 2(1-\nu)^2 + (1-\nu)] + 1$$
$$B = 3[1-(1-\nu)(1-\alpha)] - (1+\alpha)k$$
$$x = \frac{\sigma(\mathrm{I})}{\sigma_{\mathrm{eff}}} \qquad (\sigma_{\mathrm{eff}} = \rho_{\mathrm{eff}}^{-1}). \tag{3}$$

From (3) it follows that $B = 0$ and $k = 3\nu_c$ for $\alpha = 0$ at the critical point where $x = 0$. Thus, setting $\nu_c = 0.17$, we find the fitting parameter $n = 15$. It is noteworthy that numerical calculation methods give $\nu_c = 0.15$–0.19 [11] for various continuum problems of the percolation theory. Coefficient $B \cong 0$ for $\alpha \neq 0$ and $\alpha \ll 1$ at the critical point, where topological properties of the system change abruptly and an infinite domain of the high-conductivity phase is formed. Taking this circumstance into account, we can obtain an analytical expression for the conductivity at the critical point, which is valid at $\alpha < 0.1$ (figure 2).

$$x_c = \sqrt{\frac{\alpha(1-\nu_c)}{\nu_c}} \cong 2.2\sqrt{\alpha} \qquad (\nu_c = 0.17). \tag{4}$$

Figure 3 shows the ratios $\sigma(\mathrm{I})/\sigma_{\mathrm{eff}}(\nu)$ and $\sigma_{\mathrm{eff}}(\nu)/\sigma(\mathrm{II})$ as functions of the relative volume fraction of the high-conductivity phase II for two limiting cases: $\sigma(\mathrm{II}) = \infty$, superconductor; curve 1 and $\sigma(\mathrm{I}) = 0$, insulator; curve 2. In both cases $\alpha = 0$. The calculations were performed using formula (3).

Thus, in addition to the known threshold parameters and critical coefficients of the percolation theory, $\nu_c = 0.17$, the critical index of infinite cluster density $\beta = 0.4$ and the critical index of electrical conductivity $t = 1.7$ (figure 2), the threshold resistivity is introduced for describing polymorphic transformation in solids under high pressure. Also, it is proposed to regard the corresponding pressure $P = P_c$, where $x = x_c$, as the phase transformation pressure. Far from the percolation threshold ($\nu > 0.5$), the dependence $\sigma(\nu)$ is linear (figure 2), in agreement with the estimates made in terms of the effective-medium method.

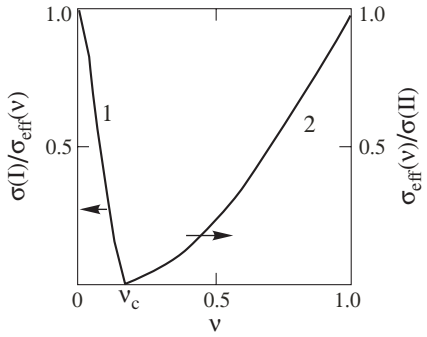

Figure 3. Dependence of $\sigma(\mathrm{I})/\sigma_{\mathrm{eff}}(\nu)$ ($\sigma(\mathrm{II}) = \infty$, superconductor; curve (1)) and $\sigma_{\mathrm{eff}}(\nu)/\sigma(\mathrm{II})$ ($\sigma(\mathrm{I}) = 0$, insulator; curve (2)) on the relative volume fraction of the high-conductivity phase II.

Figure 1 presents the results of a quantitative analysis of the experimental data for n-HgTe [2], p-PbTe [3] and n-InAs [4]. It is seen that the threshold pressures P_c are as follows (GPa): 1.6 in n-HgTe, 6.5 in p-PbTe [3] and 6.9 in n-InAs.

3. Conclusion

It is clear that the proposed HSEM model is universal and can be applied to a mathematical description of various heterophase systems on the basis of conductivity data. Furthermore, the effective-medium approximation yields erroneous results in the range $\nu_c < \nu < 0.4$ and the percolation theory is applicable at the percolation threshold, whereas expression (3) can be used at $0 < \nu < 1$ and $0 < \alpha < 1$. It is proposed to define the pressure $P = P_c$, at which $\sigma_{\mathrm{eff}}(\nu)/\sigma(\nu) = \sigma_{\mathrm{eff}}(\nu_c)/\sigma(\nu)$, as the phase transition pressure, which is important for pressure metrology.

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