

Bitransitions in two-level disordered systems

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(Presented by Academician I. M. Lifshitz, March 23, 1976)

(Submitted March 17, 1976)

Dokl. Akad. Nauk SSSR **235**, 82-85 (July 1977)

PACS numbers: 64.60.Cn

The existence of bitransitions, i.e., pairwise-generated phase transitions of the first kind, has recently been predicted in nonsymmetric disordered systems with a short-range pairwise interaction^{1,2}; they did not exist in symmetric systems.³ The purpose of this communication is to report the results of studies which show that in the general case of systems with interactions of an arbitrary nature, bitransitions as well as triple transitions exist not only in nonsymmetric but also in symmetric disordered systems and that the possibilities of realizing bitransitions are expanding significantly.

As a particular example of a system which we shall consider below for definiteness, we take superionic crystals which can go over into a state of anomalously high ionic conductivity (superionic state) as a result of disordering of one of the sublattices (usually, a cation sublattice). In nonsymmetric systems the number N' of energy-equivalent interstitial positions in a crystal does not coincide with the number of sites N in the disordered sublattice.

In the average-field approximation (Bragg-Williams, Curie-Weiss), which, as is well known, describes the general character of the behavior of the systems quite effectively,^{4,5} the free energy associated with the disordering effect is of the form

$$F(n) = Wn - \frac{\lambda}{N} f(n) - T \ln \left[\frac{N!}{n!(N-n)!} \frac{N'!}{n!(N'-n)!} \right] - nT \ln \chi; \quad (1)$$

here n is the number of defects, i.e., the number of cations which have moved from their own sites to interstitial sites; $W > 0$ is the energy formation of one defect in the absence of interactions in the system; $\lambda > 0$ is a phenomenological constant describing the interaction of the defects with each other; other; $f(n)$ determines the dependence of the interaction on the defect concentration. The third term in Eq. (1) describes the contribution of the configurational entropy and the fourth term takes account of the changes in the character of the vibrations of a cation as it passes from its site to an interstitial site. In the simplest case, χ does not depend on T ($0 < \chi < \infty$);

see, for example, Yu. Ya. Gurevich.⁶ In the case of a short-range pairwise interaction (nearest-neighbor approximation), we have $f(n) = n^2/(2N^2) = x^2/2$, where $x = n/N$.

The form of $f(x)$ may change significantly if the contribution from other interactions is taken into account. Below we consider a quite broad class of functions $f(x)$ which satisfy two obvious conditions $f(0) = f'(0) = 0$ (these conditions correspond to the fact that a term, linear in x , which describes an ideal system without interactions has already been isolated in F) and the monotonicity condition for $f'(x)$, i.e., $0 < x < 1$. The monotonicity condition is not very restrictive and, at the same time, even for such a simple class of functions $f(x)$ it is possible to obtain a number of new nontrivial singularities in the behavior of a system.

Since, as shown by analysis, for $f(x)$ of any character there is no fundamental difference in the behavior of symmetric ($N' = N$) and nonsymmetric ($N' \neq N$) systems, we shall study the case $N' = N$. Going over to a dimensionless concentration x of defects in Eq. (1), we obtain

$$\frac{1}{N} F(x, T) = Wx - \lambda f(x) - T[x \ln \chi - 2x \ln x - 2(1-x) \ln(1-x) + 2]. \quad (2)$$

From the condition $\partial F / \partial x = 0$ we obtain the equation of state of the system,

$$\frac{T}{\lambda} = \frac{\tilde{x} - f'(x)}{\ln[(1-x)^2 \chi / x^2]}, \quad (3)$$

where $\tilde{x} = W/\lambda$, $0 < \tilde{x} < \infty$.

In particular ranges of the dimensionless parameters x and χ , Eq. (3) has only one solution for some values of T and three solutions for other values of T ($0 \leq x_1 \leq x_2 \leq x_3 \leq 1$); the possibility of phase transitions existing between x_1 and x_3 (x_2 is unstable) corresponds to this. In the

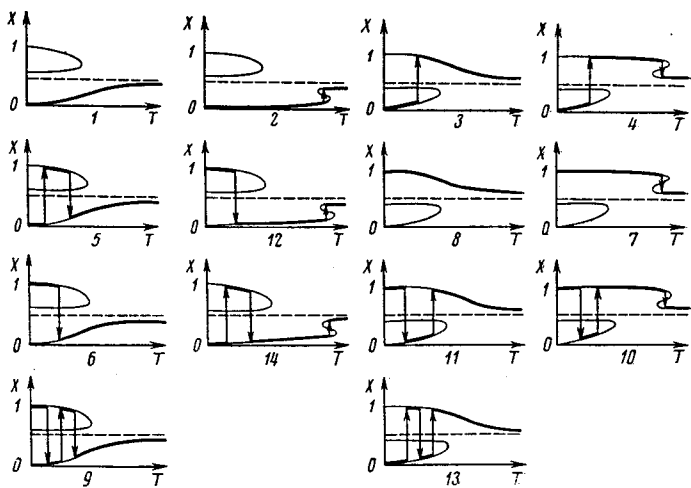


FIG. 1

general case, the function $x(T)$ defined by Eq. (3) is depicted by two curves: 1) a loop-shaped curve connecting the solution which, for $T \rightarrow 0$, emerges from the point x_0 where $\tilde{x} = f'(x_0)$ (if, of course, the solution of this equation, which is unique by virtue of the monotonicity of $f'(x)$, is contained within the limits of the physical interval $0 < x_0 < 1$) with the solution that emerges from $x = 0$ or $x = 1$ as $T \rightarrow 0$; 2) the branch that emerges from $x = 1$ or $x = 0$, respectively, as $T \rightarrow 0$ and tends to the asymptote $x_\infty = \sqrt{\chi}/(1 + \sqrt{\chi})$ as $T \rightarrow \infty$ (see Fig. 1). The loop can lie both above and below the second branch of $x(T)$, depending on the ratio between x_∞ and x_0 . In the plane of parameters $\tilde{x}$ and χ the condition $x_\infty = x_0$ determines the curve $\chi_l(\tilde{x})$ which emerges from the origin and tends to the asymptote $\tilde{x} = f'(1) \equiv a$. Regions to the left of $\chi_l(\tilde{x})$ correspond to the loop lying below the second branch of the curve $x(T)$ and regions to the right of $\chi_l(\tilde{x})$, to the loop lying above the second branch.

S-shaped segments on which phase transitions should occur can be formed on the second branch of the curve $x(T)$. The conditions for their occurrence are

$$\frac{\partial F}{\partial x} = 0, \quad \frac{\partial^2 F}{\partial x^2} = 0, \quad \frac{\partial^3 F}{\partial x^3} = 0. \quad (4)$$

Conditions (4) determine in the plane of the parameters $\tilde{x}$ and χ a critical curve of the onset of phase transitions on

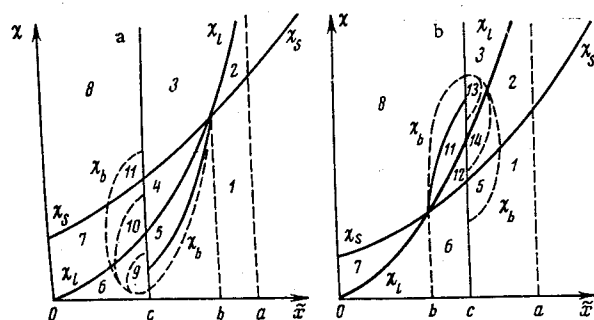


FIG. 2

S-shaped segments of the function $x(T)$:

$$\chi_s(\tilde{x}) = \chi_* \exp[\xi(\tilde{x} - b)], \quad (5)$$

where

$$b = f'(x_*), \quad \chi_* = x_*^2/(1 - x_*)^2, \quad \xi = 2/f''(x_*)x_*(1 - x_*).$$

and x_* is the solution of system (4), which we shall assume to be unique.

The uniqueness condition for the solution of Eq. (4), a condition which is not essentially restrictive for the class of functions $f(x)$, is necessary here to illustrate the simplest case of system behavior. No difficulty is encountered in generalizing the results to the case when several solutions of the system (4) exist. S-shaped segments on the curve $x(T)$ exist in regions on the parameter plane which extend to the left of $\chi_s(\tilde{x})$ for $\tilde{x} > b$ and to the right of $\chi_s(\tilde{x})$ for $\tilde{x} < b$. It is easily seen that $\chi_l(\tilde{x})$ and $\chi_s(\tilde{x})$ intersect at $\tilde{x} = b$, $\chi = \chi_*$. We introduce one more condition determining the system behavior at low temperatures. For $\tilde{x} > c$, where $c \equiv f(1)$, as the initial state (possessing minimum free energy) we have $x = 0$, and for $\tilde{x} < c$, we have $x = 1$. Note that the variants $b > c$ (Fig. 2a) and $b < c$ (Fig. 2c) are possible.

Finally, let us examine the possibility of bitransitions being realized on loop-shaped segments of the function $x(T)$. Tangency of the two branches of the curve $F(x(T), T)$ proves to be the condition for the formation of these segments:

$$F(x_1(T), T) = F(x_2(T), T),$$

$$\frac{d}{dT} F(x_1(T), T) = \frac{d}{dT} F(x_2(T), T), \quad \frac{\partial F}{\partial x} = 0. \quad (6)$$

Conditions (6) determine in the parameter plane a critical curve of the formation of bitransitions $\chi_b(\tilde{x})$. This curve emerges from the point $\tilde{x} = b$, $\chi = \chi_*$, where "weak" bitransitions ($x_3 - x_1 \ll 1$) arise, and reaches the point $\tilde{x} = c$, $\chi = 1$, in whose neighborhood "strong" bitransitions ($x_3 - x_1 \approx 1$) arise. The character of the behavior of the curve $\chi_b(\tilde{x})$ in the neighborhood of $(\tilde{x}) = c$, $\chi = 1$ can be studied from the equation for the strong-transition temperature, which is obtained from the condition $F(x_1, T) = F(x_3, T)$, Eqs. (2) and (3), and the condition $x_1 \ll 1$, $1 - x_3 \ll 1$:

$$\lambda(\tilde{x} - c) = T \ln \chi - 2T\chi^{1/2}e^{-\lambda\tilde{x}/2T} + \lambda f''(1)\chi^{-1/2}e^{-\lambda(a-\tilde{x})/2T}. \quad (7)$$

The shape of the curve $\chi_b(\tilde{x})$ depends essentially on the relation which arises between $a/2$ and c when the last two terms on the right-hand side of Eq. (7) are compared at $\tilde{x} \approx c$. In the case of a short-range pairwise interaction, $f(x) = x^2/2$, $a/2 = c = 1/2$, i.e., accidental degeneracy occurs. In the general case, $a/2 \neq c$ and, as shown by analysis of the solutions of Eq. (7), when $b > c$ the curve $\chi_b(\tilde{x})$ can either lie entirely to the right of $\tilde{x} = c$ or reach the point $\tilde{x} = c$, $\chi = 1$ from the region $\tilde{x} < c$ in one of three ways, indicated by dashed lines in Fig. 2a. When $b < c$, the curve $\chi_b(\tilde{x})$ either lies entirely at $\tilde{x} < c$, or reaches the point $\tilde{x} = c$, $\chi = 1$ from the region $\tilde{x} > c$ in one of three ways, indicated by dashed lines in Fig. 2b. At the same time, the plane of the parameters $\tilde{x}$, χ may be di-

vided into 14 regions by critical curves χ_1, χ_5, χ_b and the vertical line $\tilde{x} = c$. (Only part of them can be realized simultaneously; see Fig. 2.) The functions $x(T)$ and scheme of phase transitions as T increases that correspond to each region are shown by diagrams 1-14 in Fig. 1.

As is seen from Fig. 1, the equation of state (3) gives four variants of the function $x(T)$ (diagrams 1-4), which differ as to the position of the loop above or below and the presence or absence of an S-shaped segment. When there is an S-shaped segment (diagrams 2, 12, 14, 4, 7, and 10), phase transitions certainly occur in the system, the number of these transitions being 1 (diagrams 2, 7) 2 (diagrams 12, 4) and 3 if there are bitransitions (diagrams 14, 10). In the absence of an S-shaped segment, the phase transitions may be absent (diagrams 1, 8) or their number may be 1 (diagrams 6, 3) and if bitransitions occur, 2 (diagrams 5, 11) and 3 (diagrams 9, 13).

In the case of the short-range pairwise interaction $f(x) = x^2/2$ the parameter b coincides with c and the regions 4, 5, 9-14, in which multiple phase transitions occur in the symmetric ($N' = N$) system under consideration,

contract to the point $\chi = 1, \tilde{x} = 1/2$. Thus, accidental degeneracy, because of which bitransitions and multiple transitions are absent in the system when $f(x) = x^2/2$ and $N' = N$, is removed either with a change in the shape of the function $f(x)$ or with the introduction of a nonsymmetric $N' \neq N$. Since the relation often used for the short-range pairwise interaction $f(x) = x^2/2$ is the simplest approximate model, there is reason to hope that bitransitions should be realized in a broad class of systems with interactions of various characters.

The author expresses his profound gratitude to Academician I. M. Lifshitz for his useful comments and to Yu. Ya. Gurevich, R. R. Dogonadze, and A. M. Kuznetsov for their detailed discussion of the paper.

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Translated by R. C. Hutchison

Reconstruction of the parameters of a pulsed distribution from experimental data on the annihilation of positrons using statistical methods

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(Submitted March 24, 1977)

Dokl. Akad. Nauk SSSR, **235**, 313-316 (July 1977)

PACS numbers: 06.50.Dc, 78.70.Bj

1. Success in applying statistically based methods to processing experimental data used to establish the specific physical properties of a medium in positron diagnostics^{1,2} is governed to a large extent by the effectiveness of the computational procedure in searching for an extremum of a many-variable function (the residual sum of squares).

In the present paper it is shown, using an example of establishing the parameters of the pulsed density distribution function $\rho(p)$ of annihilating electron-positron pairs, that it is possible to make effective use of a modified Newton-Raphson, Hartley linearization method.^{4,5} A drawback of the traditional linearization method is the fact that the convergence depends on the choice of the initial approximation for the required parameters.^{5,6} The modified method described in the present paper is free from this drawback.

We considered the problem of establishing the function $\rho(p)$ from a curve of the angular correlation in Stewart's approximation,^{3,7} when the connection with the counting-rate function $J(\alpha)$, measured as a function of the

angle α , has the form

$$J(\alpha) = A \int_{|\alpha|}^{\infty} \rho(p) p dp. \quad (1)$$

Equation (1) corresponds to the geometry of long slits: $p_{\max} \ll 2\Delta = l/d$ ($p_{\max}$ is the maximum pulse of the distribution in units of m_{ec} , d is the distance between the specimen and the detector, l is the length of the slit, and A is a constant which depends on the geometry of the experiment).^{8,9} The experimental counting-rate function can be written in the form $J^e(\alpha_1) = J(\alpha_1) + \delta_1$, where δ_1 is a normally distributed random quantity with a mathematical expectation of zero. Using model representations of the nature of the interaction of positrons in metals, we will assume that the function $J(\alpha)$ can be represented in the form of the sum of a parabola and a Gaussian function

$$J(\alpha) = \varphi(\alpha) + \theta_s \exp[-\theta_s(\alpha + \theta_s)^2], \quad p_s^2 = \theta_s/\theta_2. \quad (2)$$