

Double phase transition

D. G. Sannikov

Institute of Crystallography, USSR Academy of Sciences

(Submitted 1 February 1980)

Pis'ma Zh. Eksp. Teor. Fiz. **31**, No. 6, 342–344 (20 March 1980)

A phase transition resulting from a merging of two, second-order and first-order transitions in the region of intersection of their lines in the phase diagram, is examined. The anomalies of the physical values obtained as a result of such transition differ substantially from those resulting from the usual, first-order phase transition.

PACS numbers: 64.60. – i

Two phase transitions in close proximity to each other on the temperature-pressure phase diagram can combine into one phase transition. Such unification or fusion of the transitions occurs without fail if at least one of them is a first-order transition (close to the second transition). The fusion is attributable to anharmonic interaction of the normal coordinates which are the order parameters of these transitions (for specificity, we shall discuss the structural phase transitions of the displacement type). In other words, the spontaneous values of the normal coordinates of one mode, which are obtained as a result of the first-order transition, renormalize the elastic constant of the other mode due to the interaction. As a result, there is a simultaneous loss of stability of the crystal relative to the coordinates of both modes. The stronger is the interaction of the normal coordinates, the longer is the line of such double transition in the phase diagram. We shall examine, therefore, the lowest, third-order anharmonic interaction, which is realized most readily for the normal coordinates according to the one-dimensional (P) and two-dimensional (η, ξ) representations of the symmetry group of the original phase of the crystal. If the one-dimensional representation is contained in the vector representation, then P will represent the component of the polarization vector. Using for η and ξ the conventional polar coordinate system $\eta = \rho \cos \phi$ and $\xi = \rho \sin \phi$, we write the thermodynamic potential in the form

$$\Phi = \alpha P^2 + \beta P^4 + \gamma P^6 + A \rho^2 + B \rho^4 + B' \rho^4 \cos 4\phi + a P \rho^2 \sin 2\phi - PE. \quad (1)$$

Suppose that $\beta < 0$, $\gamma > 0$, $B' > 0$, $B - B' > 0$ and for specificity $a > 0$. Note that by using the term $(\eta^2 - \xi^2)P = P\rho^2 \cos 2\phi$ instead of the interaction term $2\eta \xi P = P\rho^2 \sin 2\phi$, we obtain the same results, if the sign of the B' coefficient is changed.

The phase diagram, which corresponds to the potential (1), is shown in Fig. 1 in terms of the variables α/α_0 and A/A_0 , where $\alpha_0 = \beta^2/\gamma$ and $A_0 = (-\beta/\gamma)^{1/2}a$. The diagram varies as a function of a single dimensionless parameter $b = (B - B')/B_0$, where $B_0 = a^2\gamma/\beta^2$ ($b = 1/2$ in Fig. 1). The three phases are stable if $B' > 0$. The original phase 0 corresponds to the solution $P = 0$, $\rho = 0$; phase 1, the polar phase, corresponds to the solution $P \neq 0$, $\rho = 0$; and phase 2 corresponds to the solution $P \neq 0$, $\rho \neq 0$, $\cos 2\phi = 0$. The line between the points *I* and *II* with the coordinates *I* (1/4, $1/\sqrt{2}$) and *II* ($1/4\beta + 1/4, 0$) is the line for the double transition between the phases 0

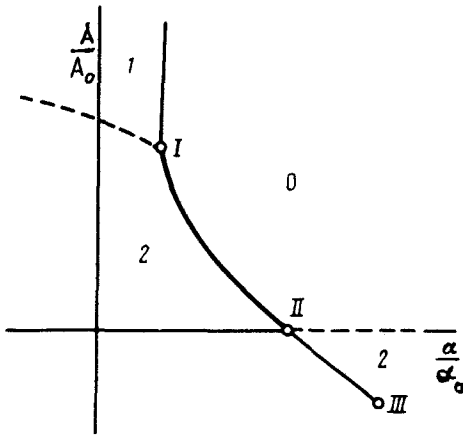


FIG. 1.

and 2. At the triple points *I* and *II* this line breaks up into two lines of the phase transitions. The lines of the first-order ferroelectric transitions 0-1 ($\beta < 0$) and of the second-order transition 1 = 2 diverge at point *I* (if $b \gg 1/4$). The lines of the improper, second-order ferroelectric transition 0 = 2 ($b > 0$) and of the isostructural, first-order phase transition 2-2 diverge at point *II* which ends at point *III* ($1/4 \beta + 3/5, -32\beta/25\sqrt{5}$).

The anomalies of the physical values for the double transition differ substantially from those for the ordinary, first-order transition. We shall examine the dielectric susceptibility $\chi = dP/dE$. Let us assume that only the coefficient $\alpha = \alpha_T(T - \theta)$ changes, and the *A* coefficient is constant. The difference between the double transition 0-2 and the ordinary transition 0-1 increases with increasing distance of the former from the triple point *I* at which these transitions are contiguous to each other. We shall take, therefore, the limiting value $A = 0$. Figure 2 shows the anomaly χ/χ_0 , where $\chi_0 = \gamma/\beta^2$ at $A = 0$ for the three different values $b = 1, 1/3$ and $1/5$. The smaller is the value of *b*, the greater is the difference between the χ anomaly and the ordinary anomaly. For values of $b < 1/3$ χ experiences an abrupt change in the upward direction rather than downward as a result of the transition. We note that the polarization jump is independent of *b* in the transition: $P^2(-\beta/\gamma) = 1/2$ (at $A = 0$).

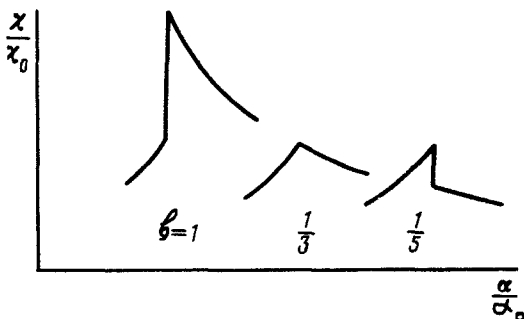


FIG. 2.

As the experimental data indicate, the double phase transitions occur in many crystals. As a result of a phase transition from the cubic phase to the rhombic phase, the dielectric susceptibility in boracites experiences an abrupt change in the downward direction (see, for example, Ref. 1) as well as in the upward direction.² The shape of the curves in Fig. 2 agrees well with that of the observed curves. We should emphasize that the double transition may occur as a result of variation of the A coefficient rather than the α coefficient, or both of them. In this sense, we must not consider as the order parameter only the P variable or only the η and ξ variables in the case of the double transition. By varying both the α and A coefficients, we increase the possibility of explaining the anomalies in the double transitions in the specific cases. In the case of the boracite crystals the concept of the double transition allows us to understand the large variety of the heretofore unexplainable anomalies observed as a result of the phase transition from the cubic to the rhombic phase.

¹J. Albers, R. W. Sailer, and H. E. Muser, Phys. Stat. Sol. a**36**, 189 (1976).

²H. Schmid and L. A. Petermann, Phys. Stat. Sol. a**41**, k 147 (1977).