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SECOND ORDER PHASE TRANSITION IN SODIUM NITRATE

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IN the theory of phase transitions[1] a body is usually considered isotropic with respect to its elastic properties, and is characterized by a single modulus of compressibility. But the behavior of the elastic constants of a monocrystal may exhibit various properties in a second order phase transition which are strongly related to specific types of structural changes of the crystal lattice at the transition point. It would hardly be reasonable to investigate this problem in general, in view of the very large number of possibilities that may arise.

We here consider a second order phase transition in sodium nitrate. Kornfel'd and Chudinov[2] have recently measured the temperature dependence of the elastic constants of this substance in the neighborhood of the transition point.

The $NaNO_3$ crystal is rhombohedral. Below the transition point its elementary cell contains two molecules, and the NO_3 groups have two different crystallographic orientations (symmetry group D_{3d}^6; see Wyckoff's[3] description). Above the transition point there is no difference between the NO_3 groups, each of which can have one of two possible orientations with equal probability.[4] This reduces the elementary cell by a factor of two (symmetry group D_{3d}^5). Thus the transition is related to ordering the NO_3 groups.

In the present case the density function $\rho(x, y, z)$, which enters into the general theory of second order phase transitions, can be thought of as the density distribution of oxygen atoms. Using the general methods[1,5] one can show that the change $\delta\rho(x, y, z)$ of the density function corresponding to the given transition has the same symmetry as the function $\sin \pi(x + y + z)$, where x, y, and z are the coordinates relative to the axes of the rhombohedral cell. Therefore the transition being considered in sodium nitrate is described by a single parameter η which transforms as the functions $\sin \pi(x + y + z)$ under all transformations of the symmetry group D_{3d}^5 of the high-temperature phase (including translations).*

From this it follows immediatedly that in the series expansion for the thermodynamic potential there will be no term proportional to η^3, so that the transition may indeed take place as a second order transition.

To determine the change of the elastic constants at the transition point, we write the thermodynamic potential in the neighborhood of this point in the form

$$\begin{aligned}\Phi = \Phi_0(T) + A(T - T_c)\eta^2 + {}^1/_2 B\eta^4 + a\eta^2(\sigma_{xx} + \sigma_{yy}) + b\eta^2\sigma_{zz} - \alpha_1(T - T_c)(\sigma_{xx} + \sigma_{yy}) - \alpha_3(T - T_c)\sigma_{zz} \\ - {}^1/_2 s_{11}(\sigma_{xx}^2 + \sigma_{yy}^2 + 2\sigma_{xy}^2) - {}^1/_2 s_{33}\sigma_{zz} - {}^1/_2 s_{44}(\sigma_{xz}^2 + \sigma_{yz}^2) - s_{12}(\sigma_{xx}\sigma_{yy} - \sigma_{xy}^2) - s_{13}(\sigma_{xx} + \sigma_{yy})\sigma_{zz} \\ - s_{14}[(\sigma_{xx} - \sigma_{yy})\sigma_{zz} - 2\sigma_{zx}\sigma_{xy}],\end{aligned}$$

where σ_{ik} is the elastic strain tensor, and T_c is the transition temperature in the absence of strain; we have here accounted for the rhombohedral symmetry of the elastic properties of the crystal, and the specific symmetry of the parameter η. The phase transition occurs at the point at which the coefficient of η^2 vanishes, i.e., at the temperature

$$T_c' = T_c - (a/A)(\sigma_{xx} + \sigma_{yy}) - b\sigma_{zz}/A.$$

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*The parameter η may be defined as $(w_1 - w_2)/(w_1 + w_2)$, where w_1 and w_2 are the probabilities for the two orientations of the NO_3 group at some lattice site.

Determining η^2 from the condition that the thermodynamic potential be a minimum when $T < T'_c$, and inserting this into the expression for Φ, we obtain the potential of the low-temperature phase, namely

$$\Phi = \Phi_0(T) - (A^2/2B)(T-T_c)^2 - (\alpha_1 + aA/B)(T-T_c)(\sigma_{xx}+\sigma_{yy}) + (\alpha_3 + bA/B)(T-T_c)\sigma_{zz} -$$
$$- {}^1\!/_2(s_{11}+a^2/B)(\sigma_{xx}^2+\sigma_{yy}^2+2\sigma_{xy}^2) - {}^1\!/_2(s_{33}+b^2/B)\sigma_{zz}^2 - {}^1\!/_2 s_{44}(\sigma_{xz}^2+\sigma_{yz}^2) - (s_{12}+a^2/B)(\sigma_{xx}\sigma_{yy}-\sigma_{xy}^2) -$$
$$- (s_{13}+ab/B)(\sigma_{xx}+\sigma_{yy})\sigma_{zz} - s_{14}[(\sigma_{xx}-\sigma_{yy})\sigma_{zz} - 2\sigma_{zx}\sigma_{xy}],$$

from which we can immediately determine the discontinuities in the elastic coefficients at the transition point,

$$\Delta s_{11} = \Delta s_{12} = a^2/B, \quad \Delta s_{33} = b^2/B, \quad \Delta s_{13} = ab/B, \quad \Delta s_{14} = \Delta s_{44} = 0,$$

and the discontinuities in the coefficients of thermal expansion

$$\Delta\alpha_1 = aA/B, \quad \Delta\alpha_3 = bA/B.$$

Although the coefficients s_{14} and s_{44} have no discontinuities at the transition point, they have a break at this point when considered as functions of the temperature. The magnitude of this break can be found if we include terms proportional to the product of η^2 and quadratic combinations of the strain tensor components in the series expansion of the thermodynamic potential.

According to the measurements of Austin and Pierce,[6] in the temperature region we are here concerned with $\alpha_1 \sim 0.1\alpha_3$. It is reasonable to assume that the discontinuities $\Delta\alpha_1$ and $\Delta\alpha_3$ are in at least the same ratio, so that $a \lesssim 0.1b$. Then for the discontinuities in the elastic coefficients, we obtain

$$\Delta s_{11} = \Delta s_{12} \leqslant 0{,}01\,\Delta s_{33}, \quad \Delta s_{13} \leqslant 0{,}1\,\Delta s_{33},$$

which would seem to be in agreement with the results of Kornfel'd and Chudinov.

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A MEASUREMENT OF THE DEPTH OF PENETRATION OF A MAGNETIC FIELD INTO MERCURY FILMS

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MEASUREMENTS of the critical temperature and critical magnetic field were performed for mercury films whose thickness varied from 3.7×10^{-6} to 95×10^{-6} cm so as to determine the depth of penetration.

The first attempts to measure this depth of penetration were those of Appleyard, Brostow, H. London, and Misener[1] in films, Shoenberg[2] in colloidal samples, Desirant and Shoenberg[3] in thin wires, and Laurmann and Shoenberg[4] in a bulk sample. Recently the depth of penetration was measured by Whitehead[5]