Reports of the Academy of Sciences of the USSR

B. N. EGOROV, G. B. RAVICH, B. G. KRYLOV

1963

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1963. Volume 152, No. 2

PHYSICAL CHEMISTRY

B. N. EGOROV, G. B. RAVICH, B. G. KRYLOV

SECOND-ORDER PHASE TRANSITION IN 2,4,6-TRINITROPHENOL

(Presented by Academician I. V. Tananaev on May 6, 1963)

The properties of many-particle systems, primarily thermodynamic functions, in the vicinity of a second-order phase-transition point constitute one of the most interesting problems in the physics of condensed media (^{1}). The well-known thermodynamic theory of Landau and the application of group theory made it possible to establish a number of general regularities obeyed by second-order phase transitions (^{2}). However, for many specific cases—especially in organic substances—the connection of these phenomena with intramolecular motion is still unclear. To resolve this question it is necessary to accumulate data on the phenomenological description of second-order transitions, on the basis of which deeper studies of these phenomena can be developed.

In connection with our systematic investigations of phase transformations in solid organic substances, the thermal expansion of several nitro compounds was studied; as a result, second-order phase transitions at low temperatures were found in several molecular crystals.

This article describes experimental data for 2,4,6-trinitrophenol, obtained on a linear dilatometric apparatus with a mechanoelectronic sensor of small displacements. The measurement results were recorded automatically on an electronic potentiometer.

The initial samples were prepared by pressing, at a pressure of 10000 kg/cm^2 and at a temperature of 100°C, a polycrystalline substance that had been repeatedly recrystallized. Under such preparation conditions the density of the samples obtained is close to that of a single crystal and is 1.75 g/cm^3. Measurements were carried out in the temperature interval from 55°C to the temperature of liquid nitrogen. The experimental results were well reproducible. All dilatograms obtained on cooling at rates from 0.2 to 6.4 deg/min had an identical form. A typical dilatogram of trinitrophenol at a cooling rate of 0.2 deg/min is shown in Fig. 1. It is seen from the figure that at temperatures from 55 to 10° the

Fig. 1. Dilatogram of 2,4,6-trinitrophenol

Figure 1: Fig. 1. Dilatogram of 2,4,6-trinitrophenol

thermal-expansion curve has a normal course, corresponding to a coefficient of linear expansion equal to 0.8—$1.1 \cdot 10^{-4}$. Upon further cooling the specific volume ceases to decrease, and at a temperature of about 0° its increase begins. With decreasing temperature this increase proceeds at an ever lower rate and ceases altogether at temperatures around -80°. Thereafter the normal course of the dilatometric curve again appears, which corresponds to thermal expansion of the substance with a coefficient of 0.06—$0.09 \cdot 10^{-4}$.

The dilatometric curve differentiated with respect to temperature, i.e., the curve of the temperature dependence of the coefficient of linear thermal expansion α, is presented in Fig. 2. The curve $\alpha = f(T)$ has a normal course in the region of low temperatures, which agrees with the theory of the solid state ([3]). Then, at temperatures from -95° to $+10^{\circ}$C, an anomalous course of α is revealed, associated with a second-order transition, and thereafter, at temperatures $10 \div 55^{\circ}$, α again acquires the usual temperature dependence, reaching a value of $0.84 \cdot 10^{-4}$ at room temperature. Extrapolation from the region of normal behavior, indicated in Fig. 2 by a dashed line, bounds the area corresponding to the thermal expansion of the substance and makes it possible to judge the magnitude of the anomalous behavior of α at low temperatures.

As can be seen from Fig. 2, the dependence $\alpha = f(T)$ in the region of the second-order transition has the form of a negative λ-point, which appears in those cases when, upon heating a substance, the second-order transition is accompanied by a decrease in specific volume. From the Ehrenfest equation $\Delta c_p = VT\frac{(\Delta\alpha)^2}{\Delta\chi}$, which establishes the relation between the jumps in the coefficient of thermal expansion $\Delta\alpha$, heat capacity Δc_p, and compressibility $\Delta\chi$ in the region of a second-order transition, it follows that second-order phase transitions may be characterized on the curves $\alpha = f(T)$ by both positive and negative λ-points. It is also evident that the corresponding curves $c_p = f(T)$ are characterized only by positive λ-points.

Fig. 1. Dilatogram of 2,4,6-trinitrophenol

It should be noted that in the literature there are very few dilatometric descriptions of second-order transitions. Most of them pertain to positive λ-points (see, for example, the second-order transition in sodium nitrate[4–6]). The second-order transition described above in trinitrophenol, together with other second-order phase transitions discovered by us in solid organic crystals, indicates a fairly wide occurrence of this type of transformation in molecular crystals, which is of great interest for the theory of phase transformations of solid organic substances.

Fig. 2. Temperature dependence of the coefficient of thermal expansion in the region of a second-order phase transition

Fig. 2. Temperature dependence of the coefficient of thermal expansion in the region of a second-order phase transition

Figure 2: Fig. 2. Temperature dependence of the coefficient of thermal expansion in the region of a second-order phase transition

In the case of molecular crystals, as is known, the molecules are held together by forces considerably weaker than those which bind the atoms in a molecule. The atoms within each molecule, in their thermal motion, oscillate relative to one another with approximately constant frequencies, which gives an Einstein-type contribution to the free energy(7,8). The onset of an anomalous temperature behavior of α (and, correspondingly, of the heat capacity) indicates the emergence of certain intramolecular processes, apparently connected with the rotation of individual groups of atoms. Direct study of these processes in organic crystals will undoubtedly lead to a deeper understanding of the mechanism of second-order phase transitions and will make it possible to describe them not only from the phenomenological standpoint, but also on the basis of modern achievements in the theory of the condensed state of matter.

Institute of General and Inorganic Chemistry
named after N. S. Kurnakov,
Academy of Sciences of the USSR

Received
27 IV 1963

CITED LITERATURE

1. A. A. Abrikosov, A. P. Gor' kov, I. E. Dzyaloshinskii, *Methods of Quantum Field Theory in Statistical Physics*, 1962.
2. L. D. Landau, E. Lifshitz, *Statistical Physics*, 1951.
3. R. Peierls, *Quantum Theory of Solids*, 1956.
4. F. C. Kracek, *J. Am. Chem. Soc.*, **53**, 2609 (1931).
5. J. B. Austin, R. H. H. Pierce, *J. Am. Chem. Soc.*, **55**, 661 (1932).
6. G. B. Ravich, B. N. Egorov, *ZhNKh*, **5**, 11, 2603 (1960).
7. M. Born, M. Göppert-Mayer, *Theory of the Solid State*, 1938.
8. M. Born, Huang Kun, *Dynamical Theory of Crystal Lattices*, 1958.

Note: Figure translations are in progress. See original paper for figures.