Phase transition induced in KCl by pressure at low temperatures

V. N. Laukhin, A. G. Rabin'kin and É. I. Éstrin
Institute of Chemical Physics, USSR Academy of Sciences

(Submitted February 1, 1973)
Zh. Eksp. Teor. Fiz. **64**, 2273-2276 (June 1973)

The direct (B1 → B2) and inverse (B2 → B1) transformations in KCl single crystals induced on increase and decrease of pressure are measured by the dilatometric technique in the temperature range 4.2–368°K. Both the direct and the inverse transformations take place at all temperatures down to 4.2°K. Hysteresis is observed between the direct and inverse transformations, the magnitude of which decreases upon increase in the temperature; at 4.2°K it is 11.4 kbars and at room temperature it is 3.5 kbars.

The study of phase (polymorphic) transformations at low temperatures, induced by a change in the external parameters (temperature, pressure, electric or magnetic field) is of considerable interest for the theory of phase transformations.[1] Investigations carried out over a wide range of relatively "high" (above room) temperatures have shown that thermally activated ("normal") polymorphic transformations under pressure take place with significant hysteresis between the initial direct (with increase in pressure) and inverse (with decrease in pressure) transformations, increasing rapidly with decrease in temperature.[2,3] A significant temperature dependence of the hysteresis is evidently a common characteristic of thermally activated processes.[4]

At the same time, experimental data on the course of low-temperature polymorphic transformations under pressure and on hysteresis for these transformations are practically non-existent.

In our previous research,[5] which was devoted to the phase transformation in Rb I under pressure at low temperatures, it was established that the direct transformation B1 → B2 in Rb I takes place at all temperatures studied up to 4.2°K. The problem of hysteresis of the transformation remains open, since the inverse transformation B2 → B1 does not take place in Rb I at low temperatures, and the high pressure phase is preserved (the transformation B2 → B1 develops only upon heating of the sample).

In this connection, we have undertaken a study of the polymorphic transformation under pressure in KCl, which has a higher equilibrium transition temperature (19.5 kbar at room temperature[6,7] in comparison with 4.0 kbar for Rb I). This made it possible to calculate the course of not only the direct but also the inverse transformations over the entire temperature range, down to the very lowest.

The studies were carried out on single crystals of KCl of "chemically pure" grade by the method described in[5]. The phase transformations during change in pressure were determined by a dilatometric method. The construction of the low-temperature press, of the dilatometer, of the high pressure chamber and of its calibration were described in detail in[8]. The experiments were carried out at temperatures of 368, 291, 182, 77, 50, 25 and 4.2°K. The temperature was maintained during each experiment with accuracy ± 1°. One transformation cycle was effected for each sample as follows: from the low-pressure phase with the NaCl lattice (B1) to the high-pressure phase with the CsCl lattice (B2) and inversely (B1 → B2 → B1). The beginning and end of a transformation were taken to be the pressures corresponding to the points of intersection of the straight lines obtained by extrapolation of the rectilinear portions of the dilatogram. The experimental results are summarized in the table. Examples of dilatograms obtained in the direct (B1 → B2) and inverse (B2 → B1) transformations in KCl under pressure at various temperatures are shown in Fig. 1, where the relative change in the length of the sample are plotted (in %) along the ordinate and the pressure along the abscissa.

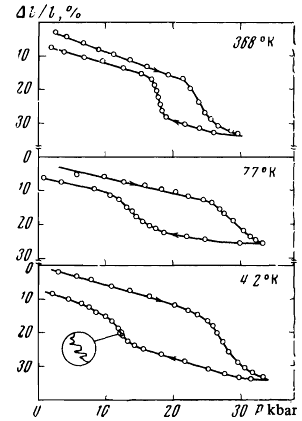

FIG. 1. Dilatograms of direct (increasing pressure) and inverse (decreasing pressure) transformations in single crystals at the temperatures 368, 77 and 4.2°K (the arrows indicate the direction of the transformation).

The experimental results show that both the direct and the inverse transformations in KCl take place at all temperatures, down to 4.2°K. The high-pressure phase is not preserved when the pressure is removed.[1)] Only at T < 50° K, as is seen from the table, are the volume effects in the inverse transformation (B2 → B1) smaller, by 2–3%, than for the direct transformation (B1 → B2), which is possibly due to the preservation of small amounts of the high-pressure phase after heating at the temperatures indicated.

Inverse (B2 → B1) transitions have a much sharper character in some experiments, i.e., they take place over a narrower range of pressures than the direct transition. At a temperature of 4.2° K, both the direct and the inverse transformations have a clearly expressed stepwise nature, while for the inverse transformation, the magnitude of the jumps is much greater (see the isolated part of the dilatogram in Fig. 1).

The low-temperature part of the T – P diagram of the transformation B1 ⇄ B2, constructed from the obtained data, is shown in Fig. 2. The equilibrium line

TABLE. Parameters of polymorphic transformation in KCl at different temperatures

T, °K	Pressure of direct transformation, kbar			Pressure of inverse transformation, kbar			Hysteresis, kbar		Volume effect of transformation, V/V, %		Equilibrium Pressure, kbar	
	beginning	middle	end	beginning	middle	end	between starts of transformations	between middles of transformations	direct transformation	inverse transformation	mean between starts of transformations	mean between middles of transformations
4.2	24.8	27.4	30.1	13.4	11.7	10.0	11.4	15.7	13.2	8.4	19.1	19.6
25	25.1	28.6	32.2	14.1	11.3	8.5	11.0	17.3	11.2	8.3	19.6	20.0
50	25.4	28.0	30.6	16.3	13.8	11.3	9.1	14.2	12.4	8.5	20.9	20.9
77	24.4	27.6	30.9	16.2	13.7	11.3	8.2	13.9	9.4	9.2	20.3	20.6
182	21.7	23.7	25.7	17.6	15.7	13.8	4.1	8.0	7.8	10.1	19.7	19.7
291	21.2	23.9	26.6	17.7	16.5	15.4	3.5	7.4	10.4	11.0	19.5	20.2
368	22.0	24.0	26.2	18.5	17.8	17.1	3.5	6.2	11.1	11.0	20.3	20.9

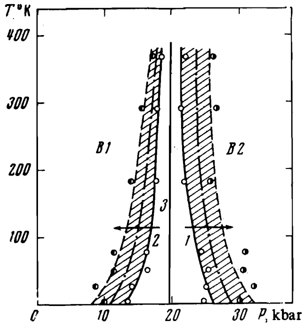

FIG. 2.

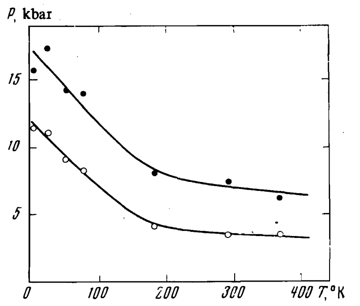

FIG. 3.

FIG. 2. T–P diagrams of the transformation B1 ⇌ B2 in KCl at low temperatures: 1 – beginning of the direct (B1 → B2) transformation with increase of pressure; 2 – beginning of inverse transformation (B2 → B1) with lowering of pressures; 3 – lines of equilibrium of phases B1 and B2, constructed as the mean between the starts of the direct and inverse transformations. The points ◑ and ◐ are the ends of the direct and inverse transformations, respectively; the dot-dash lines are the mean positions of the direct and inverse transformations. The shaded region is the region of development of the transformations.

FIG. 3. Temperature dependence of the hysteresis of the transformation in KCl, determined from the starts (○) and middles (●) of the direct and inverse transformations.

calculated as the mean line between the pressures at the beginning of the direct and inverse transformations, are practically vertical over the entire temperature range; the mean (over all data) equilibrium transition pressure is $P_0 = (20.1 \pm 0.9)$ kbar, which agrees with the data in the literature.[6,7]

By affecting the transformations in both directions we were able to establish the temperature dependence of the hysteresis: the hysteresis of the transformation in KCl increases regularly from 3.5 kbar at 368° K to 11.4 kbar at 4.2° K (Fig. 3).[2)] The general character of the temperature dependence of the hysteresis in the low-temperature region is similar to that established previously[2-4] in other materials at higher temperatures. Judging from the shape of this dependence, the pressures of the direct and inverse transformations as T → 0 should not differ essentially from the values obtained at 4.2° K.

Thus, as a result of the investigations that we carried out, it is established that a polymorphic transformation takes place under pressure in KCl at all temperatures down to 4.2° K. Hysteresis (in pressure) is observed between the direct and inverse transformations, and its value decreases systematically with increase in temperature. The character of the temperature dependence of the hysteresis permits us to assume that the transformation in KCl can take place even at lower temperatures.

Attention is directed to the similar character (already noted in[3]) of the temperature dependence of the hysteresis and the yield point (of critical cleavage stresses), which also increase as the temperature is lowered (see, for example,[9]). It is not excluded that there exists a strong connection between hysteresis and the yield point (which determines both the maximum nonrelaxing elastic energy developed in the material in the formation of the crystal or the nucleus of the new phase, and the beginning of mass motion of the dislocations that take part in the transformation).

The course of the transformations at temperatures close to 0° K, where the possibility of thermally activated surmounting of the potential barriers to the stage of formation and growth of crystals of the new phase is excluded, means either the disappearance of barriers for sufficient thermal stimulation of the transformation (i.e., the loss of stability of the crystal lattice of the initial phase relative to motion of the boundary separating the phases[10]) or the surmounting of the barriers through quantum effects.[1] To clarify these problems, and also problems on the origin of the temperature dependence of the hysteresis, a further detailed study of the low-temperature transformations is necessary in materials that differ in nature (metals, covalent crystals, etc).

[1)] Comparison of the behavior of Rb I[5] and KCl shows that, for similar materials, the preservation or nonpreservation of the high-pressure phase upon removal of the pressure is determined both by the magnitude of the hysteresis and by the absolute value of the equilibrium pressure of the transition, P_0; the higher P_0, the smaller the probability of preservation of the high-pressure phase, under otherwise equal conditions.

[2)] These values refer to hysteresis determined between the starts of the direct and inverse transitions. As is seen from Fig. 3, the general character of the temperature dependence of the hysteresis remains the same for any method of determination of the value of the hysteresis.

[1] I. M. Lifshitz and Yu. Kagan, Zh. Eksp. Teor. Fiz. **62**, 385 (1972) [Soviet Phys.-JETP **35**, 206 (1972)].

[2] Yu. S. Geishaft, L. D. Livshitz and Yu. N. Ryabinin, Zh. Tekh. Fiz. **37**, 179 (1967) [Soviet Phys.-Technical Physics **12**, 126 (1967)].

[3] T. I. Petrunina and E. I. Estrin, Dokl. Akad. Nauk SSSR **183**, 817 (1968) [Soviet Phys.-Doklady **13**, 1243 (1969)]; V. I. Soshinkov, T. I. Petrunina and E. I. Estrin, Kristallografiya **17**, 423 (1972) [Soviet Phys.-Crsytallogr. **17**, 367 (1972)].

[4] E. I. Estrin, Fiz. Tverd. Tela **13**, 1501 (1971) [Soviet Phys.-Solid State **13**, 1259 (1971)].

[5] V. N. Laukhin, A. G. Rabin'kin and E. M. Estrin, Fiz. Tverd. Tela **14**, 1800 (1972) [Soviet Phys.-Solid State **14**, 1551 (1972)].

[6] A. J. Darnell and W. A. McCollum, J. Phys. Chem. Solids **31**, 805 (1970).

[7] L. D. Livshitz, Yu. N. Ryabinin, L. V. Larionov and D. S. Zverev, Zh. Eksp. Teor. Fiz. **55**, 1173 (1968) [Soviet Phys.-JETP **28**, 612 (1969)].

[8] D. V. Alymov, V. N. Laukhin, A. G. Rabin'kin and S. A. Smirnova, Prib. Tekh. Eksp. No. 1, 185 (1972).

[9] A. I. Roĭtburd, Collection (Sbornik): Imperfections of Crystal Structure and Martensitic Transformations (in Russian) Nauka, 1972, p. 7.

[10] V. S. Bobrov, E. Yu. Gutmanas and V. P. Kisel', Collection (Sbornik): Physical Processes of Plastic Deformation at Low Temperatures (in Russian), Naukova dumka, Kiev, 1973.

Translated by R. T. Beyer
242