The Influence of Hydrostatic Pressure on the Phase Transition Temperature of Ferroelectric Crystals of the KH_2PO_4-Type

By

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The shift of the transition temperature with pressure for KH_2AsO_4 ($dT_c/dp = (-3.3 \pm 0.2)$ deg/kbar) and for RbH_2PO_4 ($dT_c/dp = (-8.2 \pm 0.3)$ deg/kbar) was determined by dielectric-constant measurements under hydrostatic pressure up to 1.2 kbar. The experimental data are analysed using a formula for the shift of T_c with pressure derived from Kobayashi's theory.

Aus dielektrischen Messungen unter hydrostatischem Druck bis zu 1,2 kbar wurde die Druckverschiebung der Umwandlungstemperatur für KH_2AsO_4 ($dT_c/dp = (-3.3 \pm 0.2)$ grd/kbar) und für RbH_2PO_4 ($dT_c/dp = (-8.2 \pm 0.3)$ grd/kbar) bestimmt. Die experimentellen Daten werden auf der Grundlage einer Formel für die Druckverschiebung der Umwandlungstemperatur, diskutiert die aus der Theorie von Kobayashi abgeleitet wurde.

1. Introduction

KH_2PO_4 is the most typical substance among a group of hydrogen-bonded ferroelectrics. If hydrogen is substituted by deuterium, the transition temperature increases strongly, which has stimulated the experimental and theoretical work on KH_2PO_4 and KD_2PO_4. The influence of hydrostatic pressure on the phase transition of these substances was determined from neutron scattering by Umebayashi, Frazer, Shirane, and Daniels [1]; from dielectric-constant measurements on KD_2PO_4 by Samara [2], and on KH_2PO_4 by Hegenbarth and Ullwer [3]. Based on the tunneling model [4, 5], theoretical investigations on the influence of pressure on the phase transition have been made by Novaković [6] in the molecular-field approximation and by Blinc and Žekš [7] in the cluster approximation of Blinc and Svetina [8].

These authors explained the shift of the transition temperature with pressure in KH_2PO_4 and KD_2PO_4 thereby emphasizing the great importance of the tunneling motion of the hydrogen isotope in the $O–H \cdots O$ bonds for the understanding of the isotope effect.

It is of interest to know how the other constituents of the lattice influence the phase transition and the ferroelectic behaviour. For this reason we measured the dielectric constant as a function of temperature under hydrostatic pressure up to about 1.2 kbar for KH_2AsO_4 and RbH_2PO_4 within the region of phase transition.

From the equation for T_c in Kobayashi's theory for KH_2PO_4-type ferroelectrics [9, 10] we derived a closed expression for the shift of T_c with pressure.

With the aid of this formula, the measuring results are discussed and numerical values for the parameters of the tunnelling model are determined.

2. Experimental

Pressure was generated with the thermal-compressor method. Helium gas was used as the pressure-transmission medium. The apparatus is described in [11]. The pressure was determined by a Bourdon-type manometer to an accuracy of $\Delta p = \pm 16$ bar. For temperature measurement a platinum resistance thermometer was used. The single crystals we received from the Physics Institutes of the Czechoslovakian Academy of Sciences in Prague and the Polish Academy of Sciences in Poznań. The KH_2AsO_4 crystals had a surface of about 30 mm² and a thickness of about 1 mm, and the RbH_2PO_4 crystals were 80 mm² and 1.7 mm, respectively. Silver and gold electrodes have been evaporated under high vacuum. The capacity was measured at a frequency of 800 Hz, at an electric field strength $E < 20$ V/cm for KH_2AsO_4 and $E < 8$ V/cm for RbH_2PO_4, respectively.

3. Results

Fig. 1 and 2 show the anomalies of the dielectric constants in the phase transition region for a KH_2AsO_4 and a RbH_2PO_4 crystal. In both cases, by

Fig. 1. Temperature dependence of the dielectric constant under different pressure for a KH_2AsO_4 crystal in the phase-transition region (10³ at = 0.981 kbar). Curves 1 to 4: measured with decreasing temperature; curves 1′ and 5: measured with increasing temperature
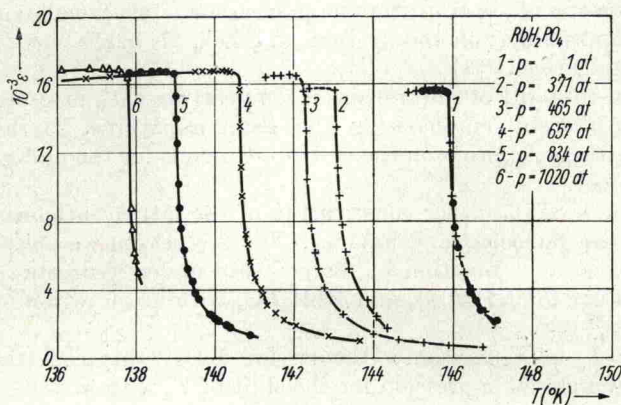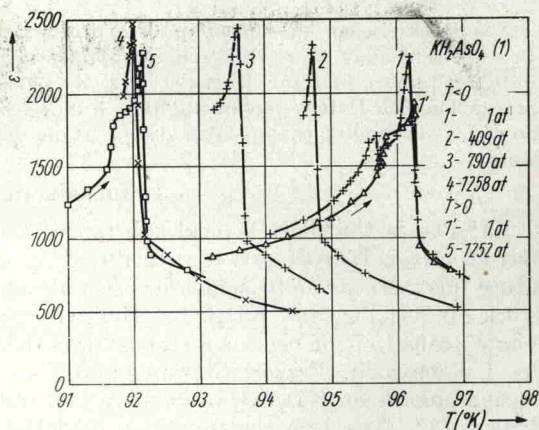

Fig. 2. Temperature dependence of the dielectric constant under different pressure for a RbH_2PO_4 crystal in the phase-transition region, measured with decreasing temperature