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On the Pressure Dependence of the Ferroelectric Properties of KH_2PO_4 and KD_2PO_4

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(25. II. 68)

Abstract. The dependences of the ferroelectric Curie temperatures (T_C), spontaneous polarizations and the Curie-Weiss constants of KH_2PO_4 and KD_2PO_4 on hydrostatic pressure have been evaluated within the protonic order-disorder model, using a four particle cluster approximation. The order of magnitude and sign of the pressure effects as well as the direction of the isotope shifts agree rather well with the recent experimental data of Umebayashi, Frazer, Shirane, Daniels and Samara.

Umebayashi, Frazer, Shirane and Daniels [1] have recently shown that the ferroelectric Curie temperatures (T_C) of KH_2PO_4 and KD_2PO_4 decrease with increasing hydrostatic pressure and Samara [2] found a similar decrease for the Curie-Weiss constant of KD_2PO_4. These data are in marked contrast with the case of triglycine sulphate [2b] where pressure induces a shift of the Curie point towards higher temperatures. The most interesting result of these studies however, is the discovery

of a striking isotope effect in the T_C pressure coefficients: $|dT_C/dp|$ is about 1.7 times smaller [1] in KD_2PO_4 then in KH_2PO_4. Since the elastic stiffness coefficients at constant electric displacement seem to be practically identical [3] for undeuterated and deuterated crystals of the KH_2PO_4 family, this large isotope effect seems to reflect the differences in the microscopic details of the ferroelectric transition mechanisms in the deuterated respectively undeuterated compounds and might be thus helpfull in checking the various theoretical models proposed so far [4–12].

In view of the well known isotope effects in the Curie temperature, the shape of the polarization curve, the saturation value of the spontaneous polarization and the domain wall dynamics on replacing hydrogen by deuterium in KH_2PO_4, it has been suggested [10] that the SLATER-TAKAGI-SENKO-UEHLING model [4–8] of ferroelectricity in this compound should be combined with the so-called tunneling model [9] to take into account the overlap of the protonic wave functions between the two sites in the hydrogen bond. The purpose of the present paper is to find out whether the newly discovered isotope effects in the pressure dependence of the dielectric properties are consistent with this combined model and whether they can be reproduced by the same set of parameters as used for the description of the other equilibrium properties of this system.

In the above mentioned «combined» model which was worked out in a four [10] and a seven particle cluster approximation, the equilibrium properties depend [10] on two primary and two secondary parameters: the Slater short range configuration energy ε and the tunneling matrix element Γ, as well as the energy of a H_3PO_4 defect w and the long range dipole-dipole interaction energy γ. The values of these parameters and the derivatives of the Curie temperatures with respect to them are collected in Table I. Since the Curie temperatures are relatively insensitive to small changes in w, the variations of w with pressure will be neglected and T_C will be assumed to depend on pressure only through ε, Γ and γ:

$$T_C(p) = T_C[\varepsilon(p), \Gamma(p), \gamma(p)] .$$

In evaluating the pressure dependences of these parameters we shall further assume that the principal effect of pressure is to reduce the O–H—O distance since the hydrogen bond is the softest bond in the crystal. A reduction in the O–H—O distance reduces the separation between the two potential minima in the H-bond and slightly increases the O–H distances. In the first approximation this last increase can be neglected and the whole effect of pressure can be reduced to the decrease in the width 2ζ of the potential barrier, separating the two protonic equilibrium sites.

Table I

Parameters used to describe the equilibrium dielectric properties of KH_2PO_4 and KD_2PO_4 in Ref. [10] and derivatives of T_C with respect to them ($T_0 = 220°$ K).

	$\varepsilon/k\,T_0$	$\Gamma/k\,T_0$	$w/k\,T_0$	$\gamma/k\,T_0$	$\frac{\partial(T_C/T_0)}{\partial(\varepsilon/k\,T_0)}$	$\frac{\partial(T_C/T_0)}{\partial(\Gamma/k\,T_0)}$	$\frac{\partial(T_C/T_0)}{\partial(w/k\,T_0)}$	$\frac{\partial(T_C/T_0)}{\partial(\gamma/k\,T_0)}$
KH_2PO_4	0.27	0.83	4.1	0.1064	1.44	− 0.30	0.07	2.11
KD_2PO_4	0.525	~0	4.1	0.1064	1.24	− 0.02	0.03	2.12

For the pressure dependence of the Curie temperature one thus obtains

$$\frac{dT_c}{dp} = \frac{\partial T_c}{\partial \varepsilon}\frac{d\varepsilon}{dp} + \frac{\partial T_c}{\partial \Gamma}\frac{d\Gamma}{dp} + \frac{\partial T_c}{\partial \gamma}\frac{d\gamma}{dp} \tag{1}$$

where – as we will see – $\gamma = \gamma[a(p), \zeta(p)]$, $\varepsilon = \varepsilon[\zeta(p)]$, $\Gamma = \Gamma[\zeta(p)]$ and where the pressure dependence of ζ can be expressed in terms of the changes in the unit cell edge a and these in terms of the known [14] elasticcompliance constants s_{ij} or elastic stiffness coeficients c_{ij}:

$$\frac{d\zeta}{dp} = \frac{1}{4}\, a \left(\frac{1}{a}\frac{da}{dp}\right) = -\frac{1}{4}\, a\, S_x \tag{2}$$

with

$$S_x = S_y = (s_{11} + s_{12} + s_{13}) = \frac{c_{13} - c_{33}}{2\,c_{13}^2 - (c_{11} + c_{12})\,c_{33}} = 0.99 \times 10^{-3}/\text{kbar} \tag{3}$$

as first pointed out by NOVAKOVIĆ [11].

Similarly one gets

$$S_z = 2\, s_{13} + s_{33} = 1.16 \times 10^{-3}/\text{kbar} \tag{4}$$

and

$$\frac{1}{V}\frac{dV}{dp} = -\,(S_x + S_y + S_z) = -\,3.14 \times 10^{-3}/\text{kbar}\,. \tag{5}$$

Since the derivatives of T_C with respect to ε, Γ and γ are easily obtained from Ref. [10] – Table I –, all one still has to do is to find the dependence of ε, Γ and γ on ζ and a.

As mentioned in Ref. [10], a simple electrostatic calculation indicates that in first order ε is proportional to ζ^2. Thus one finds

$$\frac{d\varepsilon}{d\zeta} = \frac{2}{\zeta}\,\varepsilon \tag{6}$$

and

$$\frac{d\varepsilon}{dp} = \varepsilon\,\frac{a}{2\zeta}\left(\frac{1}{a}\frac{da}{dp}\right). \tag{7}$$

The «bare» tunneling matrix element Γ_0 has been shown [15] to be given by

$$\Gamma_0 = \frac{2\,E_0\,q\,e^{-q^2}}{1 - e^{-2q^2}}\left[q\,(1 - H(q)) + \frac{1}{\sqrt{\pi}}\,(1 - e^{-q^2})\right] \tag{8}$$

where $q^2 = 2\,m\,E_0\,\zeta^2/\hbar^2$, $H(q) = (2/\sqrt{\pi})\int_0^q e^{-t^2}\,dt$, and E_0 is the zero point energy of the particle with a mass m. In the limit of a high potential barrier, $q^2 \gg 1$, this expression reduces to

$$\Gamma_0 \approx E_0\,\frac{2}{\sqrt{\pi}}\,q\,e^{-q^2}\,. \tag{9}$$

The proton, however, does not move in a rigid lattice and the proton-lattice coupling renormalizes [16] Γ_0, so that

$$\Gamma = \Gamma_0\, e^{-\sum_k f(\omega_k)} = \Gamma_0\, A\,. \tag{10}$$

A realistic calculation of A is rather difficult [16], but it seems that in a first approximation A does not depend on pressure. Thus one finds

$$\frac{d\Gamma}{d\zeta} = -\frac{\eta}{\zeta}\Gamma \tag{11}$$

and

$$\frac{d\Gamma}{dp} = -\Gamma\frac{\eta}{2}\frac{a}{2\zeta}\left(\frac{1}{a}\frac{da}{dp}\right) \tag{12}$$

where $\eta \approx 2q^2 - 1$. Using the zero point energies from the infrared data and $2\zeta_H = 0.35$ Å [17], $2\zeta_D = 0.40$ Å – assuming a small expansion of the H-bonds on deuteration [18] – one finds $E_{0,H} = 1250\ \text{cm}^{-1}$, $E_{0,D} = (1/\sqrt{2})\,E_{0,H} = 885\ \text{cm}^{-1}$, $q_H^2 = 2.29$, $q_D^2 = 4.23$, so that $\Gamma_{0,H} \approx 215\ \text{cm}^{-1}$ and $\Gamma_{0,D} \cong 30\ \text{cm}^{-1}$. A comparison of these values with the ones obtained from a best fit of the dielectric and thermal properties (Table I) yields $A \sim 0.6$.

The long range interaction energy parameter γ consists of two parts:

$$\gamma = \gamma_1 + \gamma_2$$

where γ_1 measures the direct proton-proton (or better H-bond) dipolar interactions ($\gamma_1 \propto (\zeta^2/a^3)$) and γ_2 stands for the indirect lattice mediated proton-proton coupling and is proportional to $(\zeta/a^3)^2$ as shown in Ref. [10].

Thus

$$\frac{1}{\gamma_1}\frac{d\gamma_1}{dp} = \left(1 - 3\frac{2\zeta}{a}\right)\frac{a}{2\zeta}\left(\frac{1}{a}\frac{da}{dp}\right) \tag{13a}$$

$$\frac{1}{\gamma_2}\frac{d\gamma_2}{dp} = \left(1 - 6\frac{2\zeta}{a}\right)\frac{a}{2\zeta}\left(\frac{1}{a}\frac{da}{dp}\right). \tag{13b}$$

Since $(2\zeta/a) \ll 1$, the right hand sides of (13a) and (13b) are practically equal, thus yielding the same pressure dependence. The relative magnitudes of the contributions of γ_1 and γ_2 to γ are therefore not important and one may, for sake of simplicity, take $\gamma_1 = \gamma_2$. Adding up the various contributions one gets

$$\frac{dT_c}{dp} = \left[\left(\frac{\partial T_c}{\partial \varepsilon}\right)\varepsilon - \left(\frac{\partial T_c}{\partial \Gamma}\right)\Gamma\frac{\eta}{2} + \left(\frac{\partial T_c}{\partial \gamma}\right)\gamma\alpha\right]\frac{a}{2\zeta}\left(\frac{1}{a}\frac{da}{dp}\right) \tag{14}$$

where $\alpha = 1 - (9/2)\cdot 2\zeta/a$. Inserting the parameters listed in Table I as well as the η and ζ values mentioned above and using $a_H = 7.45$ Å, $a_D = 7.47$ Å and Equations (2) and (3), one gets

$$\left(\frac{dT_c}{dp}\right)_H = [-1.81 - 2.07 - 0.82]\ \text{deg/kbar} = -4.70\ \text{deg/kbar} \tag{15a}$$

$$\left(\frac{dT_c}{dp}\right)_D = [-2.66 - 0 - 0.70]\ \text{deg/kbar} = -3.36\ \text{deg/kbar} \tag{15b}$$

in a surprisingly good agreement with the experimental data [1, 2]: $(dT_c/dp)_H = -4.52$ deg/kbar and $(dT_c/dp)_D = -2.63$ deg/kbar according to Ref. [1] or $(dT_c/dp)_D = -3.9$ deg/kbar according to Ref. [2], where a less completely deuterated crystal was used.

If one neglects the assumed expansion of the H-bond on deuteration and takes $\zeta_D = \zeta_H$, but keeps all other parameters fixed, one finds $(dT_c/dp)_D = -3.87$ deg/kbar.

It should be stressed that it is the larger value of the tunneling matrix element which is responsible for the larger value of dT_c/dp in KH_2PO_4 than in KD_2PO_4. If one neglects the tunneling matrix element one gets the wrong sign of the isotope effects.

The dependences of the Curie-Weiss constants C and the saturation value of the spontaneous polarization P_0 on pressure can be similarly obtained within this model in a straightforward way.

In the four particle cluster approximation one finds that in the vicinity of the Curie point the susceptibility follows a Curie-Weiss law $\chi = \varepsilon_0 C/T - T_C$ and the Curie-Weiss constant is obtained [17b] as:

$$C = \frac{2 N \mu^2}{\varepsilon_0 k} \frac{1}{f(\beta_c, \varepsilon, \gamma, w, \Gamma)} \tag{16}$$

where $\beta_c = 1/k\, T_c$, N is the number of dipoles/unit volume, μ is the dipole moment, which is proportional to ζ and where the rather complicated correction factor [17b] f measures the deviation from the Slater model. The pressure dependence of C is hence obtained as

$$\frac{1}{C}\frac{dC}{dp} = -\frac{1}{V}\frac{dV}{dp} + \frac{2}{\zeta}\frac{d\zeta}{dp} - \frac{1}{f}\left[\frac{\partial f}{\partial \beta_c}\frac{d\beta_c}{dT_c}\frac{dT_c}{dp} + \frac{\partial f}{\partial \varepsilon}\frac{d\varepsilon}{dp} + \frac{\partial f}{\partial \gamma}\frac{d\gamma}{dp} + \frac{\partial f}{\partial \Gamma}\frac{d\Gamma}{dp}\right]. \tag{17}$$

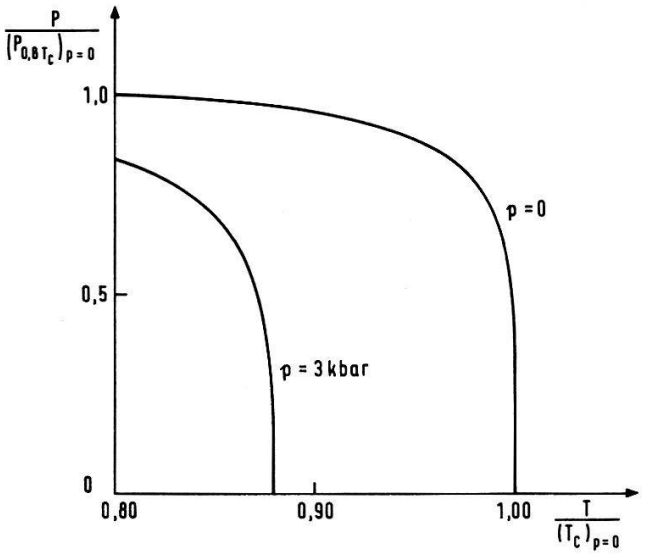
For KD_2PO_4 one thus obtains

$$\left(\frac{1}{C}\frac{dC}{dp}\right)_D = \{0.31 - 1.84 - [0.27 - 0.57 - 0.32 + 0]\}\ \%/\text{kbar} = -0.91\ \%/\text{kbar}$$

in relatively good agreement with the measured value [2] $(1/C \cdot dC/dp)_D = -1.5\%/$ kbar. If one takes $\zeta_D = \zeta_H = 0.35$ Å but again keeps all other parameters fixed, one gets $(1/C \cdot dC/dp)_D = -1.08\%/\text{kbar}$.

For KH_2PO_4 the pressure dependence of C has not yet been measured. A rough estimate yields $(1/C \cdot dC/dp)_H = -1.3\%/\text{kbar}$.

Though in the case of the pressure dependence of C the numerical agreement is not so very good as in case of the pressure dependence of the Curie temperatures, it is



Temperature dependences of the spontaneous polarization of KH_2PO_4 at zero hydrostatic pressure and at 3 kbars.

important that the sign of the pressure effects in C is correct since the positive contribution of the volume compressibility – entering through N – is more than balanced by the decrease in the dipole moments μ.

Within this model the maximum value of the spontaneous polarization, P_0, should similarly decrease with increasing pressure contrary to the situation found in guanidine aluminium sulphate hexahydrate [19]. One finds [10]:

$$P_0 = 2\,N\,\mu\,F(\varepsilon, \gamma, w, \Gamma) \tag{18}$$

where F is a function which measures the reduction in the maximum value of P_0 due to quantum effects and which reduces to ~ 1 in case of KD_2PO_4.

For KD_2PO_4 one thus gets

$$\left(\frac{1}{P_0}\frac{dP_0}{dp}\right)_D = \frac{1}{\zeta}\frac{d\zeta}{dp} - \frac{1}{V}\frac{dV}{dp} = [-0.92 + 0.31]\ \%/\text{kbar} = -0.61\ \%/\text{kbar} \tag{19}$$

whereas for KH_2PO_4 a rough estimate yields $(1/P_0 \cdot dP_0/dp)_H \approx -1\%/\text{kbar}$. Unfortunately there are no experimental data up to now to check these predictions.

Without introducing any new parameters this «combined» order-disorder model [10] is thus able to explain the sign, order of magnitude and isotope shifts of all pressure effects measured so far in addition to reproducing the equilibrium dielectric properties [10]. It is further necessary to see whether the isotope effects on replacing H by D might be as well obtained from the pure Slater model by a simple change in the configuration energy parameters without the inclusion of proton overlap. This is not the case. If one, for instance, in the simple Slater model fixes ε_H and ε_D to account for the changes in the Curie temperatures on deuteration ($\varepsilon_H = 60\ \text{cm}^{-1}$, $\varepsilon_D = 107\ \text{cm}^{-1}$) – assuming that ε increases with increasing width of the potential barrier ζ – one gets the wrong direction of the isotope effects in the T_C pressure coefficients: $(dT_C/dp)_H = -2.6$ deg/kbar, $(dT_C/dp)_D = -4$ deg/kbar. This statement is still valid in the more refined Slater model, where ε, w and γ are included: $(dT_C/dp)_H = -3.4$ deg/kbar, $(dT_C/dp)_D = -4.8$ deg/kbar.

The present results thus seem to show that whereas it is true that the configruation energy parameters depend on the width of the potential barrier and hence change on deuteration if the H-bond expands, it is the inclusion of the overlap of the proton wave functions between the two equilibrium sites in H-bond which dominates the isotope effects and without which a consistent explanation of all observed isotope effects cannot be obtained. It should be stressed, however, that the model proposed in Ref. [10] describes only the equilibrium properties and additional efforts [20–23] are needed to understand the dynamic properties as well.

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Mechanical Effects in Type II Superconductors

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(1. V. 68)

Abstract. Measurements of changes in magnetization curves under pressure and of magnetostriction in an alloy of indium with 14 at. % thallium are presented. Values for the stress dependence of the Ginzburg-Landau parameter are deduced.

Introduction

It has been known for many years that pressure influences the critical temperature and critical field of superconductors, and that there must be changes in dimensions and in elastic properties when superconductivity is destroyed. Such effects have been investigated extensively in type I superconductors [1–4], but for type II materials hardly any data exist [5, 6]. In view of the additional information to be gained from studying such materials we have made a series of observations of the changes in magnetization curves under pressures up to 14000 atmospheres in type II alloys, and we have also measured the magnetostriction occurring in the mixed state. From

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