Research Article

Calculation of the Spontaneous Polarization and the Dielectric Constant as a Function of Temperature for KH_2PO_4

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The temperature dependence of the spontaneous polarization P is calculated in the ferroelectric phase ($T < T_C$) of KH_2PO_4 (KDP) at atmospheric pressure ($T_C = 122$ K). Also, the dielectric constant ϵ is calculated at various temperatures in the paraelectric phase ($T > T_C$) of KDP at atmospheric pressure. For this calculation of P and ϵ , by fitting the observed Raman frequencies of the soft mode, the microscopic parameters of the pure tunnelling model are obtained. In this model, the proton-lattice interaction is not considered and the collective proton mode is identified with the soft-mode response of the system. Our calculations show that the spontaneous polarization decreases continuously in the ferroelectric phase as approaching the transition temperature T_C . Also, the dielectric constant decreases with increasing temperature and it diverges in the vicinity of the transition temperature ($T_C = 122$ K) for KDP according to the Curie-Weiss law.

1. Introduction

Potassium dihydrogen phosphate (KH_2PO_4 or KDP) undergoes a phase transition at $T_C = 122$ K at atmospheric pressure [1]. In the paraelectric phase ($T > T_C$) it has the space group $\bar{1}42d$ (D_{2d}^{12}), whereas in the ferroelectric phase ($T < T_C$) its space group is $Fdd2$ (C_{2v}^{19}). The paraelectric phase has the tetragonal structure with the four K- PO_4 groups in the unit cell and the tetrahedral PO_4 groups are connected by $\text{O}-\text{H} \cdots \text{O}$ bonds. In this phase the protons are randomly distributed between the two equivalent minima of the double-well potential. Below T_C in the ferroelectric phase, the protons occupy in one minima of this double-well potential so that the transition occurs by this ordering of the protons. Thus, the spontaneous polarization, which grows as the temperature decreases below T_C in the ferroelectric phase, is parallel to the c -axis and it is mainly due to the motion of the protons in KDP. This occurs when the protons tunnel from one minima of the double-well potential to the other, which is considered in the pure tunnelling model [1–5]. However, it has been considered that the proton motion couples with an optic mode of the lattice in KDP, as

studied by Kobayashi [6] in the coupled proton-optic-mode model. In the pure tunnelling model, it has been shown that the collective proton-proton tunnelling mode represents a soft mode [4], whereas in the coupled-mode model the soft mode is the lower frequency branch of the coupled system [6]. The soft mode has been observed experimentally in the Raman spectra of KDP [7–9]. At high pressures, the soft mode has also been observed experimentally in the ferroelectric phase of KDP [10]. The wavevector $\vec{q}$ dependence of the soft mode has been detected at the pressures above 40 kbar [11]. Recently, we have calculated the Raman frequency and the damping constant in KH_2PO_4 [12].

In this work, we calculate the spontaneous polarization from the observed Raman frequencies of the collective proton mode which behaves as a soft-mode response of the pure tunnelling model. By extrapolating the Raman frequencies of this mode to zero pressure, which were measured at various temperatures as a function of pressure [10] in the ferroelectric phase of KDP, the temperature dependence of the spontaneous polarization is calculated. This calculation is performed in the absence of the proton-lattice interaction for

KDP. We also calculate here the temperature dependence of the dielectric constant in the paraelectric phase of KDP using the pure tunnelling model. For this calculation, the proton-lattice interaction is also not considered and the critical behaviour of the dielectric constant is predicted close to T_C in the paraelectric phase of KDP.

Below, in Section 2, we give a theoretical outline for our calculations of the spontaneous polarization and the dielectric constant. In Section 3 we give our results. Sections 4 and 5 give our discussion and conclusions, respectively.

2. Theory

Using the microscopic theory, the mechanism of the phase transition in KDP has been explained mainly by the two models, namely, the tunnelling model of the proton and the coupled proton-optic-mode model. The ordering of the protons, which tunnels between the two minima of a double-well potential on the O-H $\cdots$ O bonds, as studied by Slater [1], causes collective proton excitations. This collective proton-proton tunnelling mode has been considered as a soft mode when the protons do not interact with the lattice [4]. Due to the fact that the spontaneous polarization (order parameter) does not have large values in this pure tunnelling model, the collective proton tunnelling mode interacts with the transverse optic mode (proton-lattice interaction) in the coupled proton-optic-mode model, as treated by Kobayashi [6]. In a previous study, the soft mode and coupled modes in the paraelectric and ferroelectric phases of KDP have been studied experimentally and the experimental results have been analyzed using both tunnelling and coupled proton-optic mode models [10]. In this study, we calculate the temperature dependence of the spontaneous polarization (order parameter) and the dielectric constant within the pure tunnelling model using the observed Raman frequencies [10] of the soft mode in KDP.

2.1. Tunnelling Model. In the tunnelling model, the proton can occupy two equivalent potential minima assigned by the pseudospin values of $\pm 1/2$. Protons can tunnel between the two minima and the energy levels of the double-well potential are separated by $\Delta E = 2\hbar\Omega$ where Ω is the tunnelling frequency.

The proton Hamiltonian H_p can be assumed to consist of a single-particle contribution and a contribution due to proton-proton interaction [3], expressed as

$$H_p = -2\Omega \sum_i S_i^x - \sum_{i,j} J_{ij} S_i^z S_j^z, \quad (1)$$

where S_i^α ($\alpha = x, y, z$) represents the α component of the pseudospin and J_{ij} is the interaction parameter between the nearest-neighbour protons. The proton Hamiltonian H_p can be solved in the mean-field approximation above the transition temperature T_C in terms of the collective proton excitation frequency Ω_0 , as given in a previous study [10],

$$\Omega_0^2 = 2\Omega(2\Omega - J\langle S^0 \rangle). \quad (2)$$

In (2) J is the Fourier transform of J_{ij} as the interaction parameter between the nearest-neighbour protons and $\langle S^0 \rangle$ is defined as

$$\langle S^0 \rangle = \frac{1}{2} \tanh\left(\frac{\Omega}{kT}\right). \quad (3)$$

As approaching the transition temperature, when there is no proton-lattice coupling, the collective excitation frequency can be assumed to disappear ($\Omega_0 \rightarrow 0$), which results in [10]

$$\frac{4\Omega}{J} = \tanh\left(\frac{\Omega}{kT_0}\right), \quad (4)$$

using (2) and (3) with the transition temperature $T \rightarrow T_0$.

According to the tunnelling model, the dielectric constant can be obtained as a function of temperature [13]

$$\varepsilon(T) = \varepsilon_L + \frac{4N\mu^2 \tanh(\Omega/kT)}{4\Omega - J \tanh(\Omega/kT)}, \quad (5)$$

where ε_L is the lattice dielectric constant independent of the temperature. The temperature dependence of the dielectric constant is governed by the second term in (5), which is the soft-mode contribution to $\varepsilon(T)$. In (5), N is the number of dipoles per unit volume and μ is the electric dipole moment.

The temperature dependence of the dielectric constant $\varepsilon(T)$ near the transition temperature T_0 in the paraelectric phase can be obtained by expanding (5) about T_0 , which gives the Curie-Weiss law expressed as

$$\varepsilon(T) \cong \frac{C}{(T - T_0)}, \quad (6)$$

where the Curie constant is defined as

$$C = \frac{16N\mu^2 k T_0^2}{(J^2 - 16\Omega^2)}. \quad (7)$$

In relation to the dielectric constant $\varepsilon(T)$, the temperature dependence of the order parameter (spontaneous polarization) can also be obtained in the tunnelling model, as given in the previous study [10],

$$P = 2N\mu\langle S^z \rangle, \quad (8)$$

where S^z represents the pseudospins directed along the z -axis. Since the spontaneous polarization (order parameter) is defined in the ferroelectric phase ($T < T_C$) only, in the paraelectric phase ($T > T_C$) $P = 0$. At very low temperatures ($T \ll T_C$), the saturated spontaneous polarization P_S is obtained as

$$P_S = N\mu \left(1 - \frac{16\Omega^2}{J^2}\right)^{1/2}, \quad (9)$$

for the pure tunnelling model [10]. In order to obtain the temperature dependence of the spontaneous polarization (order parameter), we substitute (3) into (8) since near the transition temperature $\langle S^0 \rangle$ can be replaced by $\langle S^z \rangle$ for the

pseudospins orientated along the z -axis. This then gives the temperature dependence of the spontaneous polarization as

$$\frac{P}{N\mu} = \tanh\left(\frac{\Omega}{kT}\right). \quad (10)$$

The temperature dependence of the collective proton excitation frequency Ω_0 can also be obtained by identifying it with the soft-mode response frequency w_- [4, 10]. Experimentally, the pressure dependence of w_- at constant temperatures and its temperature dependence at 6.54 kbar have been observed for KDP [10]. On the assumption that there is no proton-lattice interaction, by substituting (3) and (4) into (2) the temperature dependence of Ω_0 or the soft-mode response frequency w_- can be expressed as

$$\Omega_0^2 = 4\Omega^2 \left(1 - \frac{\tanh(\Omega/kT)}{\tanh(\Omega/kT_0)}\right), \quad (11)$$

where T_0 is the transition temperature, as before.

3. Calculations and Results

The temperature dependence of the spontaneous polarization and the dielectric constant for KDP were calculated here. For this calculation, the interaction parameter J and the tunnelling frequency Ω were determined by fitting (11) to the observed data for the soft-mode response frequency w_- at various temperatures at zero pressure [10]. The extrapolated values of the observed w_- for various temperatures at zero pressure as given in Table 1 for the ferroelectric phase of KDP [10], were used to determine the fitting parameters Ω and T_0 in (11). The fitting parameters Ω and T_0 determined are given in Table 2. In order to determine the interaction parameter J between the nearest-neighbour protons at the transition temperature, $\Omega = 54.5 \text{ cm}^{-1}$ and $T_C = 122 \text{ K}$ at zero pressure were used in (4) for KDP. The Curie constant was also determined using the J value at T_C and the Ω value according to (7) which is given as a ratio $C/N\mu^2$ in Table 2. Figure 1 gives the ratio P/P_S of the spontaneous polarization with respect to the saturated polarization which was calculated according to (9) and (10), where $\Omega = 54.5 \text{ cm}^{-1}$ was used, as a function of temperature below the transition temperature ($T_C = 122 \text{ K}$) in the ferroelectric phase of KDP. Finally, the dielectric constant $\epsilon/N\mu^2$ was calculated as a function of temperature above the transition temperature ($T_C = 122 \text{ K}$) in the paraelectric phase according to (6), as plotted in Figure 2. Here, the saturation value of the spontaneous polarization was calculated as a ratio of $P_S/N\mu$ using the Ω and J values according to (9), as given in Table 2.

4. Discussion

Using the pure tunnelling model, the temperature dependence of the spontaneous polarization P in the ferroelectric phase (Figure 1) and of the dielectric function in the paraelectric phase (Figure 2) at zero pressure was calculated here. For this calculation, the observed [10] Raman frequencies of the soft-mode, which decrease with increasing temperature at zero pressure (Table 1), were used.

FIGURE 1: Ratio of the spontaneous polarization P/P_S with respect to the saturated polarization P_S which was calculated from (9) and (10) as a function of temperature at zero pressure in the ferroelectric phase ($T < T_C$) for KDP.

FIGURE 2: The dielectric constant ϵ calculated from (6) with the Curie constant C (7) as a function of temperature at zero pressure in the paraelectric phase ($T > T_C$) for KDP.

TABLE 1: Observed values of the soft-mode response frequency w_- extrapolated at zero pressure at various temperatures in the ferroelectric phase of KDP [10].

T (K)	w_- (cm ⁻¹)
45	150.1
60	148.9
80	145.3
90	142.7

The spontaneous polarization P decreases continuously as the temperature is increased towards the transition temperature ($T_C = 122 \text{ K}$) at zero pressure (Figure 1). This is the soft-mode behaviour where the frequency decreases abruptly as the temperature approaches T_C . In fact, it has been obtained that for the pure tunnelling model the

TABLE 2: Values of the transition temperature T_C , the microscopic parameters T_0 and the tunnelling frequency Ω , interaction parameter J (see (4)), the ratio of the Curie temperature C to $N\mu^2$ (see (7)), and the ratio of the saturated spontaneous polarization P_s to $N\mu$ (see (9)) for KDP.

T_C (K)	$-T_0$ (K)	Ω (cm $^{-1}$)	J (cm $^{-1}$)	$C/N\mu^2$ (K/C $^2 \cdot$ cm $^{-1}$)	$P_s/N\mu$
122	1.35	54.5	384.6	1.65	0.824

soft mode frequency is directly related to the spontaneous polarization according to the relation

$$w = \left(\frac{J}{2\mu N} \right) P \quad (12)$$

in the ferroelectric phase of KDP [13, 14]. This indicates that the mechanism of the phase transition in KDP which is associated with the soft-mode frequency w_- , is due to the ordering of the protons in one minima of the double-well potential in this ferroelectric material.

The soft-mode response frequency w_- as it was first observed experimentally in KDP [7], is a heavily damped response centered at $w = 0$ in the Raman spectrum, as also pointed out previously [10]. The collective proton-proton tunnelling mode Ω_0 was taken here as the soft-mode response frequency w_- since Ω_0 displays a soft mode character in the absence of proton-lattice interactions [4, 10]. The temperature dependence of the soft mode frequency w_- can be described by

$$w_-^2 \propto (T - T_-), \quad (13)$$

where T_- is different from the T_C in the presence of the optic-acoustic mode interaction [10]. It has been concluded [10] that the proton motion is strongly coupled to an optic mode of the lattice so that when the protons order, the proton-lattice interaction leads to the distortion of the K-PO $_4$ sublattices to produce the spontaneous polarization in the modified tunnelling model or the coupled proton-optic mode model [6]. In regard to the proton-proton tunneling model, (13) can also be used for the proton-proton tunnelling model in the case that the proton tunnelling frequency Ω is taken as the temperature dependent.

The soft-mode response also displays a temperature dependence of the Raman frequency w_- near the transition at $T_- \approx 86$ K at a constant pressure of 6.54 kbar ($T_C \approx 91$ K), as observed experimentally in KDP [10]. It has been indicated that the difference between T_- and T_C is primarily due to the optic-acoustic-mode interaction in KDP. It has also been indicated that this transition occurs at ~ 86 K when w_- vanishes for the coupled proton-optic-mode model, whereas for the pure tunnelling model in the absence of proton-lattice interactions the proton system undergoes a transition at ~ 58 K [10]. So, the temperature difference of nearly 30 K emerges due to proton-lattice interactions at 6.54 kbar in KDP. At atmospheric pressure, our fitting parameter of T_0 (Table 2) is also about 30 K lower than $T_0 \sim 30$ K determined previously [9]. In fact, the microscopic parameter T_0 , which we obtained by fitting (11) to the observed Raman frequencies of the soft mode w_- (or collective proton excitation frequency Ω_0), was not well

determined since a large ratio of $\Omega/kT_0 > 1$ was obtained in our analysis. This gives rise to $\tanh(\Omega/kT_0) \sim 1$ which means that the fit is relatively insensitive to T_0 , as also pointed out previously for the analysis of KDP at 6.54 kbar [10]. So, the macroscopic properties of the ferroelectric materials are not well described by the microscopic parameters of the pure tunnelling model and also of the coupled proton-optic mode model, which both use the Raman data [10]. On this basis, in (4) we used the value of $T_C = 122$ K instead of the fitted parameter T_0 in the pure tunnelling model, which gave the ratio of $\Omega/kT_C = 0.64$ or $\tanh(\Omega/kT_C) = 0.57$ for KDP. Thus, the interaction parameter was determined as $J = 384.6$ cm $^{-1}$ at zero pressure in this study, which can be compared with the value of 345.1 cm $^{-1}$ at 6.54 kbar [10].

The temperature dependence of the spontaneous polarization was calculated here in the absence of the proton-lattice interactions for KDP, as stated previously. Since the spontaneous polarization does not have large values in the pure tunnelling model, the collective proton tunnelling mode can interact with the transverse optic mode (proton-lattice interaction) in the coupled proton-optic mode model introduced by Kobayashi [6], as pointed out previously [10]. The amplitude of the soft-optic mode is maximum at the phase transition temperature and there is no coupling at T_0 . Below T_0 , proton-lattice interaction can be considered to enhance the temperature dependence of the spontaneous polarization in KDP. However, the coupled mode features can disappear below T_0 in the ferroelectric phase in KDP, was also observed experimentally at approximately 30 K below T_0 in BaTiO $_3$ [15]. Thus, in the absence of the proton-lattice interaction, for the temperature dependence of the soft-mode frequency w_- (or collective proton excitation frequency Ω_0) can be described below T_0 in the ferroelectric phase of KDP.

In regard to the collective proton excitation frequency Ω_0 which was taken as the soft mode response frequency w_- for KDP as studied here, Ω_0 can also be considered as a soft mode for those ferroelectrics exhibiting displacive phase transition such as BaTiO $_3$. Soft mode in BaTiO $_3$ which consists of the vibration of Ti ions against oxygen [16] is the transverse optic mode of long wavelength at $k = 0$. Its frequency goes to zero ($w_T \rightarrow 0$) at the critical temperature T_0 and the lattice displacements associated with this mode cause the crystal distorting to the ferroelectric phase [17]. Very recently, we have investigated the temperature dependence of this soft-optic mode in ferroelectric barium titanate [18].

Using the pure tunnelling model, we also calculated the temperature dependence of the dielectric constant in the paraelectric phase of KDP, as shown in Figure 2. It decreases as the temperature increases below T_C and it diverges in the vicinity of the transition temperature

($T_C = 122$ K) according to Curie-Weiss law (see (6)). This diverging behaviour of the dielectric constant is due to the soft-mode response frequency ω_- or the collective proton-tunnelling frequency Ω_0 which vanishes as $T \rightarrow T_C$ in the pure tunnelling model of KDP. Thus, the temperature or pressure dependence of the soft-mode response frequency from the Raman spectra determines the temperature or pressure dependence of the dielectric properties of those ferroelectric materials such as KDP. Also, from the pressure dependence of the transition temperature T_C , the phase diagram calculated using proton- or-deuteron-tunnelling model [19] can be tested by the experimental Raman spectra for KDP and DKDP. Alternatively, a temperature-uniaxial pressure phase diagram of KH_2PO_4 which was obtained experimentally [20] can be calculated using the proton tunnelling model.

5. Conclusions

The spontaneous polarization P and the dielectric constant ϵ were calculated at various temperatures in the ferroelectric ($T < T_C$) and paraelectric ($T > T_C$) phases, respectively, at atmospheric pressure in KDP. The observed soft-mode frequencies from the Raman data were used to evaluate the temperature dependence of P and ϵ by the pure tunnelling model close to the transition temperature ($T_C = 122$ K) in KDP.

The critical behaviour of the spontaneous polarization P and the dielectric constant ϵ was predicted in both the ferroelectric and paraelectric phases and they can be compared with the experimental measurements. The critical behaviour of the soft-mode response frequency ω_- , spontaneous polarization P , and the dielectric constant ϵ can also be investigated at higher pressures in KDP.

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