

STRUCTURAL MECHANISM OF PYROELECTRICITY IN ZINCITE ZnO: THE RELATION BETWEEN ANHARMONIC ASYMMETRIC THERMAL VIBRATIONS AND THE PYROELECTRIC COEFFICIENTS

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ABSTRACT

The experimental value of the pyroelectric coefficient is related to the thermal vibrations determined by Kihara & Donnay (1985). It predominantly depends on the effective asymmetric anharmonic potentials of the Zn and O atoms, which are inferred from their experimentally determined asymmetric anharmonic temperature-factors.

Keywords: pyroelectricity, anharmonic asymmetric thermal vibrations, zincite.

SOMMAIRE

La valeur expérimentale du coefficient pyroélectrique est liée aux vibrations thermiques déterminées par Kihara et Donnay (1985). Elle dépend de façon prédominante des potentiels asymétriques et anharmoniques des atomes de Zn et O, qui sont déduits des facteurs de température asymétriques anharmoniques expérimentalement déterminés.

Mots-clés: pyroélectricité, vibrations thermiques asymétriques anharmoniques, zincite.

INTRODUCTION

The presence of a unique polar axis is a necessary but not sufficient condition for pyroelectric behavior in a crystalline solid. Zincite ZnO, which has a wurtzite-type structure, was chosen as a promising compound because it is strongly pyroelectric, has only one positional parameter, and has previously been studied both theoretically and in the laboratory (Table 6 in Kihara & Donnay 1985). Let us summarize the essential crystal-data: space group $P6_3mc$; $Z = 2$; Zn and O occupy Wyckoff position $2b$: $(\frac{1}{2}, \frac{2}{3}, z)$; $(\frac{2}{3}, \frac{1}{2}, \frac{1}{2} + z)$ with site symmetry $3m$, where z of Zn is set equal to zero and z of O represents the positional parameter. The equal but oppositely pointing co-ordination polyhedra about cations and anions are very slightly elongated at both 293 and 473 K (Table 5, Kihara & Donnay 1985).

A pyroelectric crystal has a static electric dipole moment. This dipole moment is usually cancelled by stray charges from its environment, such as the dust particles which, as mineral-museum curators know only too well, tend to coat pyroelectric crystals in exhibit cases. With proper precautions, we are,

however, able to obtain accurate data on the change of the dipole moment with temperature. This change, called the pyroelectric coefficient, is composed of a "primary" and a "secondary" part. The former cannot be measured directly because it requires a measurement at constant strain, which necessitates that the specimen be kept at constant volume. The secondary pyroelectric coefficient, on the other hand, results from the change in dipole moment induced by the non-zero piezoelectric coefficients and the strain caused by thermal expansion; it is measurable.

In what follows, I shall show how it is possible to correlate, on an atomic scale, the total pyroelectric coefficient with the asymmetric anharmonic thermal vibrations determined by Kihara & Donnay (1985).

RESULTS FOR ZNO

Heiland & Ibach (1966) measured the pyroelectric coefficient at constant stress for ZnO over the temperature range from 9.7 K to 420 K. They found it to be proportional to the specific heat at constant pressure and to have a value, at room temperature, of $-9.2 \times 10^{-6} \text{ C}/(\text{m}^2\text{K})$, and about $-11 \times 10^{-6} \text{ C}/(\text{m}^2\text{K})$ at 473 K, a value obtained from the extrapolation of their curve to 500 K. According to Nye (1957) the two types of pyroelectric coefficients are related by the equation

$$P_i^\sigma = P_i^\epsilon + \alpha_{jk}^E c_{jklm}^{E,T} d_{ilm}^T \quad (1),$$

where P_i^σ are the total pyroelectric coefficients measured at constant strain σ , and P_i^ϵ are the primary coefficients, α_{jk}^E are the thermal expansion coefficients at constant electric-field E , $c_{jklm}^{E,T}$ are the elastic constants at constant E and temperature T , d_{ilm}^T are the piezoelectric coefficients at constant T , and the repeated indices are summed from 1 to 3. Using the results of Tokarev *et al.* (1975) for tensors c and d , and of Kihara & Donnay [1985, eq.(5)] for α , one finds that the secondary coefficient comes out to be $-10 \times 10^{-6} \text{ C}/(\text{m}^2\text{K})$ at room temperature. This result is in reasonable agreement with the measured value of P^σ , indicating that the one non-symmetry-constrained structural parameter in ZnO, namely the z co-ordinate of the oxygen atom, has

the same value at $T = 293$ K and $T = 473$ K (Table 3, 2-c model, Kihara & Donnay 1985).

Since the source of the electric dipole moment is a separation of positive and negative charge, detailed structural measurements should be able to account for the observed pyroelectric coefficients. Such detailed measurements must take the possible anharmonic asymmetric nature of thermal vibrations into account, as was done by Kihara & Donnay (1985) in their third-order-cumulant model. The existence of these asymmetric anharmonic temperature-factors, asymmetric ATF, is well documented both theoretically (Scheringer 1985, Mair & Barnea 1975) and experimentally (Whiteley *et al.* 1978, Zucker & Schultz 1982). Using the z co-ordinates of Kihara & Donnay (1985, Table 3, 3-c model), their mean cell-volume \bar{V} for the temperature range of 293 to 473 K (their Table 1) and assuming a residual charge q of 0.5 e on the oxygen atom, we find for

$$P^{\sigma} = 2q[(zc)_{T_1} - (zc)_{T_2}] / [\bar{V}_{T_1, T_2}(T_1 - T_2)] \quad (2)$$

$$= -3.0 \times 10^{-6} \text{ e}/(\text{\AA}^2\text{K})$$

$$= -48.0 \times 10^{-6} \text{ C}/(\text{m}^2\text{K}).$$

The numerical agreement with the measured value of $-10 \times 10^{-6} \text{ C}/(\text{m}^2\text{K})$ at 383 K (Heiland & Ibach 1966) is poor, but the negative sign is correct. If the temperature-independent z co-ordinates of the 2-c model had been used, *i.e.*, the asymmetric ATF had been ignored, a positive P^{σ} of $2.5 \times 10^{-6} \text{ C}/(\text{m}^2\text{K})$ would have been obtained.

The influence of symmetric ATF can be modeled by an effective one-particle potential in which each atom vibrates at different levels for different temperatures. Following the notation of Mair & Barnea (1975), this potential can be written:

$$V(x, y, z) = V_0 + \frac{\alpha_1}{2} (x^2 - xy + y^2) + \frac{\alpha_3}{2} z^2 + \beta_1(xy^2 - x^2y) + \beta_2(x^2 - xy + y^2)z + \beta_3z^3$$

Mair & Barnea (1975) used this potential formula to obtain an expression for ATF that can be related to the one obtained with the cumulant expansion procedure (Kihara & Donnay 1985), provided the latter terms are expanded as far as the linear term in c^{ijk} . The following relations between the two sets of coefficients are then obtained:

$$\alpha_1 = \frac{8\pi^2 k_B T}{3b_{11} a^2} \quad (3)$$

$$\alpha_3 = \frac{8\pi^2 k_B T}{4b_{33} c^2}$$

$$\beta_1 = \frac{27}{128} \frac{\alpha_1^3 a^3 c^{111}}{\pi^3 (k_B T)^2} \quad (4)$$

$$\beta_2 = \frac{-9}{32} \frac{\alpha_1^2 a^2 \alpha_3 c^3}{\pi^3 (k_B T)^2}$$

$$\beta_3 = \frac{-\alpha_3^2 c^{113}}{8\pi^3 (k_B T)^2}$$

Using the cell dimensions $a = 3.249$ and $c = 5.204$ Å for $T = 293$ K and with coefficients b_{ij} and c^{ijk} taken from Kihara & Donnay (1985, Table 3), we obtain $\alpha_1 = 5.52 \times 10^{-12}$ and $\alpha_3 = 5.46 \times 10^{-12} \text{\AA}^{-2}$, $\beta_1 = 0.73 \times 10^{-12}$, $\beta_2 = 0.41 \times 10^{-12}$, $\beta_3 = 0.78 \times 10^{-12} \text{ erg } \text{\AA}^{-3}$. The above β values fall into the same range as those reported by Whiteley *et al.* (1978) for CdSe, 0.30×10^{-12} , and for ZnS, $0.67 \times 10^{-12} \text{ erg } \text{\AA}^{-3}$ for room temperature.

The one-point potential model requires the β_i values to remain unchanged with change in temperature. The data obtained at 473 K by Kihara & Donnay (1985) do not fulfill this requirement. Since their reliability is dubious, however, we cannot claim that they invalidate the one-point potential model.

With similar approximations to those used for calculating the ATF, we can calculate the thermal expansion using the relations given in equations (3) and (4). That is

$$\langle x_i \rangle = \frac{\int x_i e^{-\frac{V(x_1, x_2, x_3)}{k_B T}} dx_1 dx_2 dx_3}{\int e^{-\frac{V(x_1, x_2, x_3)}{k_B T}} dx_1 dx_2 dx_3} \quad (5)$$

Performing these integrals after linearizing $e^{-\frac{V(x_1, x_2, x_3)}{k_B T}}$ with respect to the β_1 we obtain

$$\delta a = \sqrt{\frac{8}{27}} \frac{\beta_1 k_B T}{\alpha_1^2} \quad (6)$$

$$\delta c = \frac{2}{\sqrt{3}} \frac{k_B T}{\alpha_1 \alpha_3} \left(\frac{4}{3} \beta_2 + \frac{3}{2} \beta_3 \right)$$

and with the above values, $\delta a = 1.8 \times 10^{-6} \text{ T } \text{\AA}$ and $\delta c = 1.3 \times 10^{-5} \text{ T } \text{\AA}$, where T is the temperature in Kelvin. Since there are two ZnO per cell, we obtain a thermal expansion along the c direction of $2.6 \times 10^{-5} \text{ \AA}/\text{K}$. This value should be compared with the measured value of $2.219 \times 10^{-5} \text{ \AA}/\text{K}$. We conclude that the cubic one-particle potential *can* account for a major part of the thermal expansion in the c direction, even though it neglects the interatomic couplings, which must exist.

DISCUSSION

The ideal 'harmonic crystal' is one in which atoms interact *via* a potential that is a quadratic function of the atomic displacements due to thermal motion. Such a harmonic potential leads only to symmetric, harmonic vibrations, which are correctly described by the conventional ellipsoidal temperature-factors. But we know, from elementary solid-state physics (Kittel 1971, p.218), that a harmonic crystal is an unacceptable model for a real crystal since, for example, a harmonic crystal cannot show any thermal expansion. In real crystals a relationship between pyroelectric coefficients and asymmetric thermal vibrations should not surprise us: pyroelectric coefficients can have non-zero values only in crystals whose space groups contain one unique polar axis; in such space groups all Wyckoff positions may be associated with asymmetric thermal coefficients. What is surprising, however, is that as simple a model as given by the effective one-particle potential leads to acceptable agreement with experimental thermal expansion. The author realizes, of course, that the low precision of the refinement of thermal parameters of ZnO makes the present results only semiquantitative. A more accurate thermal refinement is being undertaken by Dr. Kihara at the Photon Factory in Tsukuba, Japan, so that we should soon be able to address this issue using the improved data.

A factor that may then have to receive attention deals with the observed and statistically significant difference of $0.014 \pm 0.001 \text{ \AA}$ in bond lengths in ZnO (Kihara & Donnay 1985, Table 5), with apical bonds longer than basal bonds. The latter must be considered the more covalent ones, so that we expect higher electron-density in the basal planes of the ZnO_4 and Zn_4O tetrahedra than in the inclined planes, and that will affect the calculated intensities of (35.*l*) and (07.*l*) given by Kihara & Donnay (1985, Table 2). This effect of differential intensity becomes less pronounced whereas the effect of ATF becomes more pronounced when the angle of scattering is increased. Thus, although Kihara & Donnay (1985) did not take the difference in bond-types into account, their exclusive use of higher-order reflections in the electron-density refinement minimizes the damage done.

The original suggestion, made more than 70 years ago, that a useful relation exists between pyroelectric coefficients and thermal displacements in crystals goes back to Boguslawski (1914a, b, c). It was first tested on tourmaline by Fortier (1975), with structure refinements carried out at 193 and 293 K. In the publication of Fortier's results (Donnay 1977), attention was drawn to the atomic position of the oxygen atom O(1), the only Wyckoff position that shows a significant displacement for the 100° change in temperature and that gives unacceptably large

thermal parameters. The pyroelectric effect of tourmaline was ascribed primarily to this O(1) atomic group even though it has the highest site-symmetry, $3m$, of any of the 13 Wyckoff positions that make up the crystal structure of tourmaline. Abrahams and coworkers (1979) took exception to this interpretation, and the present author has waited for the results on ZnO before defending Boguslawski's thesis. She needed a noncentric thermal refinement of a simple crystal-structure, which would show unequivocally that there is a relation between atomic displacement and pyroelectric behavior. With the proof at hand, it appears superfluous to discuss the arguments of Abrahams *et al.* (1979) in the literature.

In summary, the atomic movements that accompany changes in temperature give rise to anharmonic asymmetric temperature-factors associated with one or more atoms in the Wyckoff positions of a given crystal-structure. These atomic displacements are related to pyroelectric behavior of the crystal. Crystals with large secondary pyroelectric coefficients are therefore excellent candidates for the study of anharmonic thermal vibrations and, conversely, meaningful structural refinements of pyroelectric crystals *must* make use of anharmonic refinement of temperature factors, at least for the atoms that move when the temperature is allowed to change. A pyroelectric crystal, like tourmaline, that had its structure refined (four times for the four principal chemical varieties: dravite, elbaite, schorl and buergerite) should have its structure refined at least once again with O(1) temperature factors not forced into ellipsoidal shape.

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