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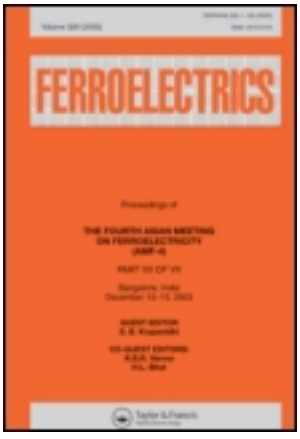

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ANALYSIS OF PYROELECTRIC AND DIELECTRIC MEASUREMENTS ON BORACITES

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Abstract-The measured temperature dependence of the dielectric constant and pyroelectric coefficient in FeI, CuCl and MnI boracites are analyzed according to the thermodynamic model advanced by Dvorak and Petzelt and by Gufan and Sakhnenko for the ferroelectric cubic-orthorhombic phase transition. A simplified form of their thermodynamic potential yields acceptable fits to the data over a large temperature interval. The values of the parameters obtained from the fits, however, are not consistent with the usual systematic neglect of high-order terms in the potential.

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INTRODUCTION

Boracites ($M_3B_7O_{13}X$, where M is a divalent metal and X is Cl, Br or I) exhibit a number of interesting structural phase transitions. Two distinct physical models have been advanced for their ferroelectric cubic-orthorhombic phase transition.

The works of Dvorak and Petzelt[1] and of Gufan and Sakhnenko[2] describe this transition with the usual Landau picture of a single structural distortion causing the full reduction in symmetry observed at the phase transition. Since the volume of the unit cell doubles at the transition point, this primary order parameter must be a zone-boundary non-polar distortion. The ferroelectricity observed in the low symmetry phase is caused by a coupling of the primary non-polar distortion to a secondary polar distortion. This model describes the boracites as improper, secondary or extrinsic ferroelectrics. Unfortunately a significant addition to this simple picture is needed to account for the decrease in the dielectric constant observed in most boracites upon transition from the paraelectric to ferroelectric phase. Namely the interaction between the primary order parameter and the secondary polarization must be extended beyond the lowest allowed by symmetry to include a second mode-coupling term.

Levanyuk and Sannikov[3] advance an alternate picture of the boracite ferroelectric transition which includes - in the spirit of Landau theory - coupling terms only of the lowest order allowed by symmetry. The unusual properties of the boracites are explained by assuming that both modes become unstable at nearly the same temperature. The non-linear coupling between the two soft modes causes the two separate structural distortions to coalese into one phase transition. Instead of two separate but close transitions - one a cell-doubling non-polar transition and the other a normal ferroelectric transition - a complex double phase transition appears. From the perspective of the softening polar mode, the coupling to the zone-boundary mode introduces a further destablizing effect which triggers the ferroelectric distortion at a temperature well before it would become unstable on its own. This picture of the boracites as triggered ferroelectrics can also account for the changes observed in the dielectric constant at the transition point.

This note summarizes the fitting of dielectric and pyroelectric measurements to the behavior predicted by the improper ferroelectric model. Measurement of the temperature dependence of the dielectric constant and pyroelectric coefficient of FeI, CuCl and MnI boracites have been made and will be reported in detail elsewhere. An examination of the dielectric data alone gave reasonable agreement with the improper ferroelectric model[4]. The pyroelectric data alone are also easily fit to this model. However, simultaneous fits of both pyroelectric and dielectric data is more demanding.

MODEL

For the improper ferroelectric model, the known space groups of the cubic and orthorhombic phases completely determine the form of the thermodynamic potential which describes the phase transition. Denoting the primary order parameter by η and the polarization by P, a simplified version of the thermodynamic potential takes the form,

$$F = F_0(T) + \alpha(T - T_0)\eta^2/2 + \beta\eta^4/4 + \gamma\eta^6/6 + P^2/2\chi_0 + a_1\eta^2P + a_2\eta^2P^2. \quad (1)$$

The temperature dependence of the spontaneous polarization, P(T), and the dielectric susceptibility $\chi(T)$, are readily obtained by the usual minimization procedure. In the ferroelectric phase this yields,

$$P = -a_1\chi_0\eta^2/(1 + 2a_2\chi_0\eta^2) \quad (2)$$

$$\chi^{-1} = \chi_0^{-1} + 2a_2\eta^2 - 2a_1^2/[(\beta + 2\gamma\eta^2)(1 + 2a_2\chi_0\eta^2)^2] \quad (3)$$

where $\eta(T)$ is determined by solving the equation,

$$\alpha(T-T_0) + \beta\eta^2 + \gamma\eta^4 - 2a_1^2\chi_0\eta^2/(1 + 2a_2\chi_0\eta^2) + 2a_2a_1^2\chi_0^2\eta^4/(1 + 2a_2\chi_o\eta^2)^2 = 0. \quad (4)$$

In the paraelectric phase, $P = \eta = 0$ and $\chi = \chi_o$ independent of temperature.

A detailed study then requires a numerical solution of equation (4). Reflection on the nature of the model and the spirit of the Landau theory suggests that a substantial simplification should be appropriate. Specifically, in this model η is sufficient to account for the phase transition alone, while the polarization is regarded as a secondary subsidiary phenomena. Thus, a reduced thermodynamic potential involving only a power series in η should be adequate to describe the temperature dependence of η near the transition. To a good approximation then, $\eta(T)$ should take the usual form for the order parameter, describing a first-order transition, namely,

$$\eta(T)^2 = \frac{2}{3}\Delta\eta^2 u(T), \text{ where } u(T) = 1 + \frac{1}{2}[(T_1-T)/(T_1-T_c)]^{\frac{1}{2}} \quad (5)$$

This approximation yields simplified expressions to compare with the data, namely,

$$p = dP/dT, \text{ where } P(T) = -b_1u(T)/[1 + b_2u(T)] \quad (6)$$

$$(\chi_o/\chi) = 1 + b_2u(T) - c_1/[1 + c_2u(T)][1 + b_2u(T)]^2$$

$$\text{where } c_2 = 1 + 3c_1b_2 - c_1 \quad (7)$$

An equivalent way to describe the same approximation is to expand the denominators in equation (4) as a power series and to retain only terms through sixth order in η. The six parameters in equations (6) and (7) can thus be related directly back to the parameters of the thermodynamic potential (1). While seven parameters appear in the

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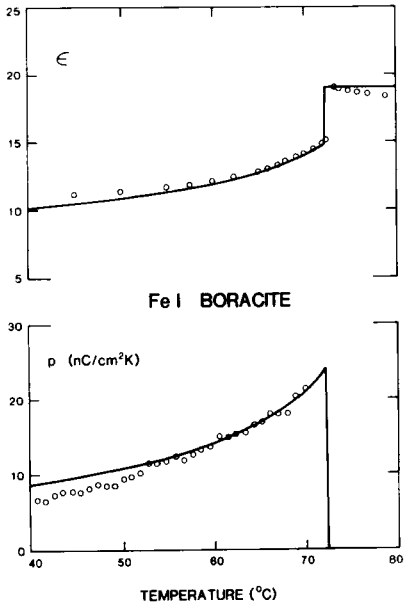

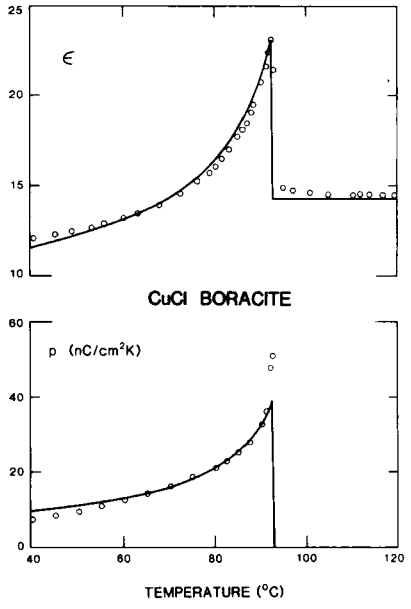

FIGURES 1,2,3 Theoretical curves fitted to the measured values of the dielectric constant and pyroelectric coefficient of FeI, CuCl and MnI boracites. The parameter values used in the fits are given in Table 1.

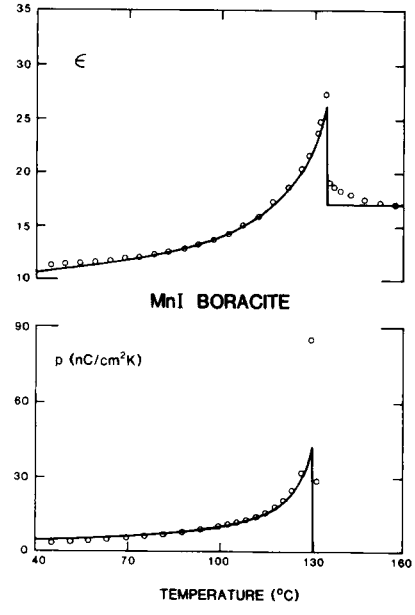

TABLE 1

	FeI	CuCl	MnI
b_1 (nC/cm^2K)	-3.7	-2.4	-1.3
b_2	0.62	0.31	0.25
c_1	-2.87	3.87	2.34
T_1 (°C)	83	100	139
T_c (°C)	72.3	93	135
χ_o	18	13.5	16

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potential, the electrical measurements provide no information on the scale of η. Thus only six degrees of freedom from the potential are in fact determined by these measurements. We are free, for example, to fix the scale of η by choosing $\gamma = 1$.

DATA ANALYSIS

The theoretical expressions contain six parameters to be determined: χ_0, b_1, b_2, c_1, T_1 and T_c. The experimental data contain only seven features to constrain the fit: T_c, p at T_c, the curvature in p below T_c, ε above T_c, the jump in ε at T_c, the curvature in ε below T_c and the value of ε far below T_c. While separate fits to the dielectric and pyroelectric data are not constrained there is just enough information in the combined measurements to provide a reasonably constrained fit. The figures illustrate the general nature of the fit; the table lists the parameter values obtained. The quality of these fits is consistent with experimental uncertainties and sample to sample variations in the data. The fits were obtained by systematically varying the parameters and comparing the resulting curves with the measurements. A balance was struck so that each of the seven features of the data noted above are reasonably represented. Because the fit is just barely constrained, a more elaborate least-squares process to obtain the parameter values and uncertainties is not appropriate. A variation in a parameter's value by a small amount (say 10%) can be compensated by adjusting the other parameters with only mild deterioration of the fit; much larger variations produce clearly unacceptable results. In summary we may conclude then that the data can be brought into reasonable correspondence with the theoretical expressions and that the parameter values are determined with only small variations.

DISCUSSION

If these fits are to be interpreted as confirming the improper ferroelectric model, certain self-consistent features must appear in the parameter values. The value of $2a_2\chi_0\eta^2 = 3b_2/2$ should be small compared with unity if the approximation used in deriving (5) is to hold. Unfortunately as we see in Table 1, the values of $3b_2/2$ are just not small. This is expected for FeI boracite because the a_2 term must be substantial to account for the jump up in ε upon heating through the transition temperature. However, MnI and CuCl boracite show a downward jump and still the a_2 term is appreciable.

Where does one go from here? First, since the approximations used in deriving the approximate temperature dependence of η are not self-consistent, one could reexamine the data using the temperature dependence of η calculated by solving equation (4). This should also yield an acceptable fit since the more accurate $\eta(T)$ will have basically the same temperature variation as the approximation used here. Second, the model of Levanyuk and Sannikov merits more attention.

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