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COMMENT

Order parameter coupling and dielectric anomaly in ammonium hydrogen oxalate hemihydrate

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Abstract. The dielectric anomaly observed at the ferroelastic transition (146 K) in ammonium hydrogen oxalate hemihydrate is shown to be due to biquadratic coupling with an incipient ferroelectric mode of ordering via a common strain. The sign of the coupling constant obtained by fitting to measured data provides evidence in support of the structural resonance theory of the pressure-induced incommensurate phase in this material recently proposed by the same author.

1. Introduction

Ammonium hydrogen oxalate hemihydrate (AHO), $\text{NH}_4\text{HC}_2\text{O}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$, has attracted interest recently because, upon cooling, it goes through an incommensurate phase only under the application of hydrostatic pressure [1]. This material has also attracted attention earlier because of the ferroelastic transition that it undergoes at 146 K (ambient pressure). One of the first indications of this low-temperature transition was the *dielectric* anomaly observed by Albers and Küppers [2]. Their dielectric constant data above, $T_a = 146$ K can be fitted to a Curie–Weiss law:

$$\epsilon_{11} = \epsilon_g + C/(T - T_c)$$

with $\epsilon_g = 5.10$, $C = 735$ K and $T_c = -20$ K. (Note that ϵ_{11} and ϵ_{22} in this paper correspond to ϵ_{22} and ϵ_{11} in [2] owing to a different setting of the axes.) This shows that AHO is an incipient ferroelectric with a would-be transition temperature of -20 K. At the ferroelastic phase transition temperature there is a collapse of ϵ_{11} . This anomaly at 146 K was treated by Albers and Küppers only as suggestive for further structural work (which Küppers and co-workers [3] subsequently performed) but was otherwise left without further comment.

We have recently shown [4] that a pressure-dependent ‘structural resonance’ between the ferroelectric degree of freedom φ and the ferroelastic degree of freedom ψ giving a term of the form

$$G_{\text{int}} = h(\varphi \nabla \psi - \psi \nabla \varphi)$$

in the free energy will account semi-quantitatively for the observed incommensurate behaviour. In this short note, we shall show that a strain-induced biquadratic coupling between these same two degrees of freedom will reproduce the observed behaviour of

ε_{11} . This coupling, then, must be included if a detailed Landau-type theory is to be successful in accounting for the whole range of experimental data collected for AHO.

2. Order parameter coupling theory

The detailed development of the theory used here has been presented by Salje and Devarajan [5].

We write the free energy as

$$G = \frac{1}{2}a\psi^2 + \frac{1}{4}B\psi^4 + \frac{1}{2}c\varphi^2 + \frac{1}{4}D\varphi^4 + E\psi^2e + F\varphi^2e + ge^2$$

where

$$a = a_0(T - T_a)$$

$$c = c_0(T - T_c)$$

with $a_0, c_0 > 0$. The first four terms are the normal Landau expansion for ψ and φ up to fourth order. The E and F terms represent the coupling to a principal strain e for each of these order parameters, while the last term is the elastic energy associated with this strain. Previous Landau theory [6] for the ferroelastic transition (ψ) has already shown that it is important to include terms of the form $e_i\varphi^2$ for the three principal strains ($i = 1, 2, 3$). Here we shall just suppose that our e is one of these three components.

Minimizing the free energy under stress free conditions ($\partial G/\partial e = 0$) gives

$$e = - (1/2g)(E\psi^2 + F\varphi^2).$$

Substituting back into the free-energy expression gives

$$G = \frac{1}{2}a\psi^2 + \frac{1}{4}b\psi^4 + c\varphi^2 + \frac{1}{4}d\varphi^4 + \lambda\psi^2\varphi^2 - h\varphi$$

where we have defined renormalized fourth-order coefficients

$$b = B - E^2/g$$

$$d = D - F^2/g$$

both of which we must assume to be positive for stability in absence of sixth-order terms, and the coupling constant

$$\lambda = - EF/2g.$$

The common strain e has led to biquadratic coupling between the order parameters ψ and φ . We have also included an extra term representing the interaction between φ and an external field h .

The different regimes of behaviours that can result are discussed in detail in [6]. Here we want to derive the susceptibility associated with φ , assuming that $T_a > T_c$.

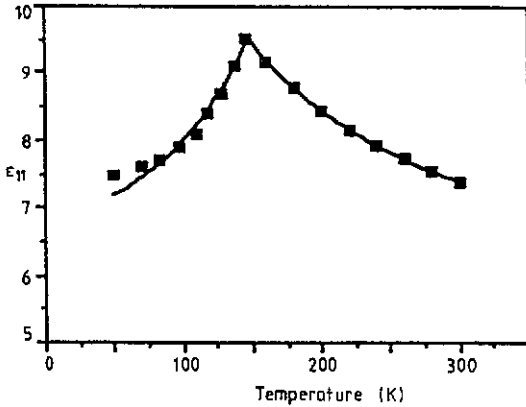


Figure 1. The measured dielectric constant ϵ_{11} (■) compared with the prediction from order parameter coupling theory (—).

(i) $T > T_a$, so that $\varphi, \psi = 0$.

$$\partial G / \partial \varphi = 0 \rightarrow \varphi(c + d\varphi^2 + 2\lambda\psi + 2) - h = 0$$

giving

$$\chi = (\partial \varphi / \partial h)|_{\varphi, \psi=0} = 1/c = 1/c_0(T - T_c).$$

(ii) $T_c < T < T_a$, wherein $\varphi = 0$ and $\psi = \sqrt{-a/b}$ (from $\partial G / \partial \psi = 0$). We similarly get

$$\chi = (\partial \varphi / \partial h)|_{\varphi=0} = 1/(c + 2\lambda\psi^2) = 1/[c_0(T - T_c) + 2\lambda a_0(T_a - T)/b].$$

3. Application to AHO

Take the two order parameters to be the ferroelastic degree of freedom ψ and the ferroelectric degree of freedom φ , so that h will be the electric field. χ can now be the dielectric constant ϵ_{11} . Taking $T_a = 146$ K, we see that above this temperature we correctly predict the behaviour of the variable part of ϵ_{11} as Curie-Weiss type. The data fitting of Albers and Küppers then gives us $c_0 = 1/735 \text{ K}^{-1}$ and $T_c = -20$ K. Below T_a we can write

$$\epsilon_{11} = 5.1 + 1/[(T + 20)/735 + \alpha(146 - T)]$$

where

$$\alpha = 2\lambda a_0/b.$$

From figure 1, we see that we can fit the experimental behaviour well down to below 70 K using the value of $\alpha = +0.004$.

4. Relevance for the pressure-induced incommensurate phase

Since a_0 and b are both positive, our result implies that the coupling constant $\lambda = -EF/2g$ is positive, i.e. E and F must have opposite signs (g , being an elastic constant, is positive). In other words, the ferroelectric and ferroelastic degrees of freedom in AHO

must give rise to a *compensating* common principal strain. Conversely, therefore, we expect these two ordering degrees of freedom to react in opposite ways to an externally imposed common strain, such as that resulting from the application of hydrostatic pressure. In particular, it is known that hydrostatic pressure decreases the critical temperature of the ferroelastic transition, i.e. $dT_a/dp < 0$ (see the phase diagram in [1]), in which case we can expect the ferroelectric transition to increase with pressure, $dT_c/dp > 0$.

We have recently proposed [4] a structural resonance theory to account for the occurrence of an incommensurate phase in AHO above the critical pressure of 3 kbar. A crucial assumption of our theory was that the critical temperature of the ferroelectric degree of freedom increases with pressure. The above discussion on the implication of the sign of the coupling constant λ is thus seen to provide support for the correctness of this otherwise *ad hoc* assumption.

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