PROTONIC E-MODE FLUCTUATIONS AS THE DOMINANT MECHANISM FOR ELECTRIC FIELD GRADIENTS IN KH2AsO4-TYPE CRYSTALS

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Incorporating the proton—oxygen coupled E-mode fluctuations for all wave vectors, we explain the experimental results for the temperature dependence and the effect of deuteration of the electric field gradients in KH2AsO4-type crystals.

MEASUREMENTS of electric field gradients (EFG), $V_{zz}$, are proving to be of great importance in furthering our understanding of the nature of the ferroelectric transition in KDA-type crystals. The experimental data$^1$ of $V_{zz}$ at the As site, in the paraelectric phase is well described by the formula

$$V_{zz} = AT(T - \alpha T_c)^{-1},$$

where $\alpha$ is an experimentally determined constant characteristic of a given ferroelectric and ranges typically between 0.2 to 0.45 (see Table 1). To provide a theoretical basis for equation (1), Blinc et al.$^1$ related $V_{zz}$ to the ferroelectric $B_2$-mode according to the equation

$$V_{zz} = C_B \langle \xi^2 \rangle,$$

where $\xi$ is the normal coordinate describing the $B_2$-mode. In addition, they calculated $V_{zz}$, directly, within the Slater model, and obtained an expression of the form equation (1), but with a constant $\alpha = 0.45$ for all KDP-type ferroelectrics. Further, the model of Blinc et al.$^1$ does not explain the increase in $\alpha$ upon deuteration.

Scott and Worlock$^2$ considered the effect of modes other than $q = 0$ on $V_{zz}$ and concluded that inclusion of these modes leads to qualitative agreement between theory and experiment.

In this note we consider the contribution to $V_{zz}$ of fluctuations from the protonic E-mode symmetry, hitherto neglected in theoretical considerations. This E-mode has recently been studied by Havlin et al.$^3$ From considerations similar to those given by Kobayashi,$^4$ it can be shown that there is a coupled oxygen—protonic E-mode in which the oxygens move in phase with the protons.* (see Fig. 1). By incorporating this protonic-oxygen E-mode contribution we find that our theoretical expression for $V_{zz}$ (1) is in very good agreement with theory and experiment.

Following Scott and Worlock's$^2$ procedure for evaluating $\langle \xi^2 \rangle$, we write $\langle \xi^2 \rangle$ in terms of the E-mode contribution to the susceptibility according to the relation

$$\langle \xi^2 \rangle = k_B T \int d^3q \chi_q(q, \omega = 0)n_{g}(q, T) \int d^3q \chi_q(q, T).$$

where $n_{g}(q, T) = (\exp(\beta \omega_{g}(q, T)) - 1)^{-1}$. The quantity $\chi_q(q, \omega = 0)$ was obtained recently$^5$ as

$$\chi_q(q, \omega = 0) \sim \Gamma(\tanh \beta \Gamma)/\omega^2_{g}(q, T).$$

For the regime $\beta \Gamma \ll 1$,
The central point of this paper is that the most important contribution of the E-mode fluctuation in equation (4) arises from the vicinity of the Brillouin zone boundary (Bzb) at \( q_{\text{Bzb}} \). This is to be contrasted to the dominant contribution arising from \( q \approx 0 \) for the \( B_2 \)-mode.

By taking into account the dominant contribution associated with \( q_{\text{Bzb}} \) in equation (5) and since \( J(q) \) change sign at \( q_{\text{Bzb}} \) we obtain

\[
V_{zz} = \frac{C_{\text{B}}T}{T - \gamma T_c}.
\]

We can determine \( \gamma \) from the experimental data for \( V_{zz} \) using the relation \( \chi_{\text{s}} \propto (T + \gamma T_c)^{-1} \). The available susceptibility data for CDA \(^6\) and KDA \(^7\) are shown in Fig. 2. Now, the contribution from \( q_{\text{Bzb}} \) alone already gives a value of \( \gamma \) reasonably close to experimental values \( 0.2 < \alpha < 0.45 \) (see Table 1). We can numerically take into account the contribution from all \( q \)-wave vectors. This was done by using the determined values for \( \gamma \) and the simplified expression \( J(q) = J(0) \cos(qd) \) in conjunction with equations (3)–(6). This procedure leads to excellent agreement between our theory and the experimental data for \( V_{zz} \), as shown in Fig. 2 and Table 1.

It will be noted that in the above we have completely ignored the contribution of the \( B_2 \)-mode to \( V_{zz} \). This can be understood from the fact that \( C_{\text{B}} \) and \( C_{\text{B}} \) in equation (3) depend upon the inverse cube of the distances of the Cs ions and the oxygens from the As-probe, respectively. Because of the proximity and the non-ionic nature of the chemical bond of the oxygens to the As (as compared to the large Cs–As distance) it follows that \( C_{\text{B}} < C_{\text{B}} \). It should also be noted that for KDA it is known experimentally \(^8\) that \( \chi_{\text{Cs}}(q = 0) > \chi_{\text{As}}(q = 0) \) in the major portion of the temperature range of interest here. Since \( \chi_{\text{Cs}}(q) \) increases with increasing \( q \) [equations (5), (6)] while \( \chi_{\text{As}}(q) \) decreases, \( \chi_{\text{Cs}} \) should be even more dominant near the Bzb.

The idea that the major contribution to \( V_{zz} \) at the As site comes from the protonic–oxygen fluctuations associated with the E-mode, also can explain the temperature-independent nature of \( V_{zz} \) measured at Cs site in CsH\(_2\)AsO\(_4\). \(^5\) If the \( B_2 \)-mode makes the larger contribution to \( V_{zz} \), one would expect similar temperature dependence at As and Cs sites due to their relative fluctuation. In our model, the major contribution arises from the protonic oxygen coupled E-mode which introduces asymmetry between the Cs and As ions due to the relative proximity of the oxygens to the As.

The effect of deuteration is to increase the value of \( \alpha \) in equation (1), as seen from Table 1. This can be qualitatively understood by extending the theoretical expression

\[
V_{zz} = C_{\text{D}} \frac{TT'(\tanh \beta T')}{\Gamma - \gamma \beta'(\tanh \beta T')}
\]

(which is the contribution of \( q_{\text{Bzb}} \) to \( V_{zz} \)) from above \( T_c \), to where it intersects the temperature axis. In this way one obtains for \( \beta \Gamma < 1 \)

\[
\alpha \approx \gamma - \frac{1}{3}(1 - \gamma)(\beta \Gamma)^2.
\]

However, since \( \beta \Gamma \) decreases with deuteration and \( \gamma < 1 \), it follows that \( \alpha \) increases with deuteration as found experimentally.

The differences in the value of \( V_{zz} \) for the various crystals at \( T_c \), can be qualitatively explained on the basis
of their different lattice constants. In the \( XH_2AsO_4 \)-type crystals, the lattice constants increase as \( X \) is consecutively replaced by K, Rb and Cs. It is reasonable to assume that the oxygen — As distances increase in the same manner. Since \( C_E \) in equation (3) is proportional to the inverse cube power of the distances, we expect the larger lattice constants to match the smaller \( V_{zz} \). Interchanging the protons with deuterons also increases the lattice constants, thus decreasing \( V_{zz} \). This predicted behaviour of \( V_{zz} \) is indeed borne out by experiment.\(^1\)

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**REFERENCES**