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# A THEORY OF THE ELECTRIC FIELD GRADIENT IN $KH_2PO_4$-TYPE CRYSTALS, BASED ON THE PROTONIC E-MODE

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The temperature dependence of the Electric Field Gradient in $KH_2PO_4$-type crystals is explained in terms of the $E$-mode fluctuations. Calculations based on the $q$-dependence of this mode alone lead to good agreement with the experimental data.



In recent years systematic measurements of the Electric Field Gradients (EFG), $V_{zz}$, have been performed for KDP-type ferroelectrics. Those measurements have been an important tool used to understand the nature of the ferroelectric transition. Blinc, *et al.*[1] measured $V_{zz}$ at the As-site for $KH_2AsO_4$, $CsH_2AsO_4$, $RbH_2AsO_4$ and the appropriate deuterated crystals. Their experimental data in the paraelectric phase is well described[1] by the formula

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

where $\alpha$ is an experimentally determined constant characteristic of a given ferroelectric and ranges typically between 0.2 to 0.45. An important step forward in explaining these results was made by Blinc, *et al.*[1] who related $V_{zz}$ to the ferroelectric $B_2$-mode.

According to the equation $V_{zz} = C\langle\xi^2\rangle$, 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 Eq. (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 dueteration.

Scott and Worlock[2] considered the effect of modes other than $q = 0$ on $V_{zz}$ and concluded that inclusion of these modes improves the 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. By incorporating the protonic $E$-mode contribution we find that our theoretical expression for $V_{zz}$ (i) is in very good agreement with experiment; (ii) leads to an increase of $\alpha$ with deuteration, in agreement with experiment; (iii) explains qualitatively why the temperature dependence of $V_{zz}$ measured[3] at the Cs site in $CsH_2AsO_4$ is insignificant as compared to that measured at the As site.

Including the $E$-mode contribution we can write $V_{zz}$ in a more general form

$$V_{zz} = C_B\langle\xi_B{}^2\rangle + C_E\langle\xi_E{}^2\rangle. \tag{2}$$

Following Scott and Worlock's procedure for evaluating $\langle\xi_B{}^2\rangle$, we calculate $\langle\xi_E{}^2\rangle$ in terms of the $E$-mode contribution by taking into account all the $q$ wave vector values. For the regime $\beta\Gamma \ll 1$, and $T > T_c$ the $E$-mode eigenfrequency is given by[4]

$$\omega_E{}^2(q, T) = 4\Gamma^2[T + \gamma J(q)]/T \tag{3}$$

where $\Gamma$ is the proton tunneling integral, $J(q)$ is the proton-proton interaction, and $\gamma = (\frac{1}{3})(2U_2/U_1 - 1)$, where $U_1$ and $U_2$ describe the interactions between nearest neighbour protons in the same and different $xy$-planes, respectively.

The central point of this paper is that the most important contribution of the $E$-mode fluctuation arises from the vicinity of the Brillouin zone boundary at $q = \pi/d$. 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 $q = \pi/d$ we obtain

$$V_{zz} = \frac{C_E T}{T - \gamma T_c} \tag{4}$$

Assuming $U_1 = U_2$ gives $\gamma = \frac{1}{3}$. Even this simple assumption already gives a value of $\gamma$ reasonably close to experimental[1] values $0.2 < \alpha < 0.45$. We can determine $\gamma$ from the experimental data for $\chi_x$ using the relation $\chi_x \propto (T + \gamma T_c)^{-1}$. The available susceptibility data for CDA[5] and KDA[6] are shown in Figure 1. Using the determined values for $\gamma$ and

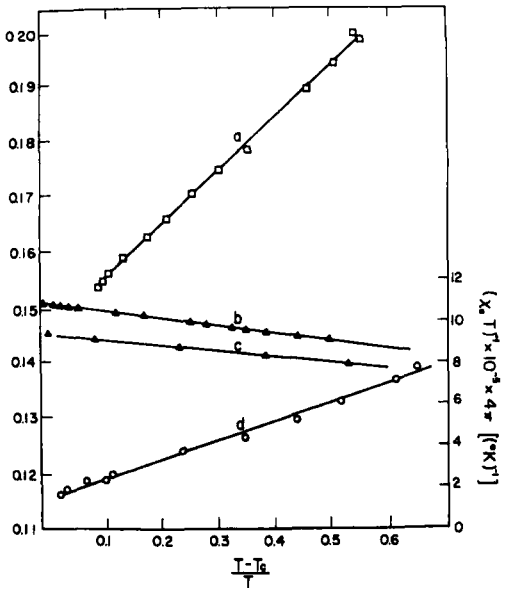


FIGURE 1 (a) and (b) describe $V_{zz}^{-1}$ and $(\chi_a T)^{-1}$ for $CsH_2AsO_4$. The points refer to the experimental data.[1,5,6] The solid lines are the predictions of the theory, calculated from Eq. (4) and Eq. (5). (c) and (d) describe the same quantities as above for $KH_2AsO_4$.

calculating numerically $\langle \xi_E^2 \rangle$ for all $q$ wave vector values, leads to excellent agreement between our theory and the experimental data for $V_{zz}$, as shown in Figure 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 $C_B$ and $C_E$ in Eq. (2) depend upon the inverse cube of the distances of the Cs ions and the protons from the As-probe. Because of the proximity and the non-ionic nature of the chemical bond of the proton to the As (as compared to the large Cs-As distance) it follows that $C_B \ll C_E$. It should also be noted that for KDA it is known experimentally[7] that $\chi_x > \chi_z$ in the major portion of the temperature range of interest here.

The idea that the major contribution to $V_{zz}$ at the As site comes from the proton fluctuations associated with the $E$-mode, also can explain the temperature-independence of $V_{zz}$ measured at Cs site in $CsH_2AsO_4$.[3] 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 fluctuations. In our model, the major contribution arises from the $E$-mode which introduces asymmetry between the Cs and As ions due to the relative proximity of the protons to the As.

As seen from experiment[1] the effect of deuteration is to increase the value of $\alpha$ in Eq. (1). This can be qualitatively understood by extending the theoretical expression

$$V_{zz} = C_E \frac{T\Gamma \tanh \beta\Gamma)}{\Gamma - \gamma J_0 (\tanh \beta\Gamma)}$$

(which is the contribution of $q = \pi/d$ to $V_{zz}$) from above $T_c$, to where it intersects the temperature axis. In this way one obtains for $\beta_c\Gamma < 1$

$$\alpha \approx \gamma - \tfrac{2}{3}(1-\gamma)(\beta_c\Gamma)^2. \qquad (5)$$

However, since $\beta_c\Gamma$ decreases with deuteration and $\gamma < 1$, it follows that $\alpha$ increases with deuteration.

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REFERENCES

1. R. Blinc and J. L. Bjorkstam, *Phys. Rev. Lett.* 23, 788 (1969); R. Blinc, M. Mali, J. Pirs and S. Zumer, *J. Chem. Phys.* 58, 2262 (1973).
2. J. F. Scott and J. M. Worlock, *Solid State Comm.* 12, 67 (1973).
3. R. Blinc and M. Mali, *Solid State Comm.* 7, 1413 (1969).
4. S. Havlin, E. Litov and H. Sompolinsky, *Phys. Lett.* 53A, 41 (1975).
5. R. J. Pollina and C. W. Garland, *Phys. Rev.* (to be published).
6. G. Busch, *Helv. Phys. Acta* 11, 269 (1938); S. Havlin, E. Litov and G. A. Uehling, *Phys. Rev.* B9, 1024 (1974).
7. I. P. Kaminow, *Phys. Rev.* 138, A1539 (1965).