Solid State Communications, Vol. 18, pp. 1357–1359, 1976. Pergamon Press. Printed in Great Britain

PROTONIC E-MODE FLUCTUATIONS AS THE DOMINANT MECHANISM FOR ELECTRIC FIELD GRADIENTS IN KH_2AsO_4-TYPE CRYSTALS

S. Havlin and Y. Yeshurun

Department of Physics, Bar-Ilan University, Ramat-Gan, Israel

(*Received* 30 *September* 1975; *in revised form* 5 *January* 1976 *by P.G. de Gennes*)

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 KH_2AsO_4-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

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

where α 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

$$V_{zz} = C_B\langle\xi_B^2\rangle \quad (2)$$

where ξ 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 α 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} (i) is in very good agreement with experiment; (ii) leads to an increase of α with deuteration, in agreement with experiment; (iii) explains qualitatively why the temperature dependence of V_{zz} measured[5] at the Cs site in CsH_2AsO_4 is insignificant as compared to that measured at the As site.

* The general problem of coupling between the protonic E-mode and the lattice vibrations, was recently discussed by Havlin and Sompolinsky (*Ferroelectrics*, in press).

Table 1. Values of α and γ [equations (1) and (6)] as determined theoretically and experimentally for the various KDA-type crystals

	γ – determined from χ_a experiments	α – calculated from theory	α – determined from V_{zz} experiments
KDA	0.30	0.22	0.22
KD*A	–	–	0.25
RDA	–	–	0.29
RD*A	–	–	0.36
CDA	0.50†	0.40	0.40
CD*A	–	–	0.43

† Though Pollina and Garland[6] fitted their data with $\gamma = 0.40$, the data can also be fitted with $\gamma = 0.50$ if the background level is taken to be $\epsilon_0^a = 13$ instead of 15.3. A value of 13 is a reasonable one for ϵ_0^a since it matches the background level below T_c.

The generalization of equation (2) including the E-mode contribution is

$$V_{zz} = C_B\langle\xi_B^2\rangle + C_E\langle\xi_E^2\rangle. \quad (3)$$

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

$$\langle\xi_E^2\rangle = k_BT\int d^3q\chi_x(\mathbf{q}, \omega = 0)n_E(\mathbf{q}, T)\Big/\int d^3q n_E(\mathbf{q}, T). \quad (4)$$

where $n_E(\mathbf{q}, T) = \{\exp\beta\omega_E(\mathbf{q}, T) - 1\}^{-1}$. The quantity $\chi_x(\mathbf{q}, \omega = 0)$ was obtained recently[3] as

$$\chi_x(\mathbf{q}, \omega = 0) \propto \Gamma(\tanh\beta\Gamma)/\omega_E^2(\mathbf{q}, T). \quad (5)$$

For the regime $\beta\Gamma \ll 1$,

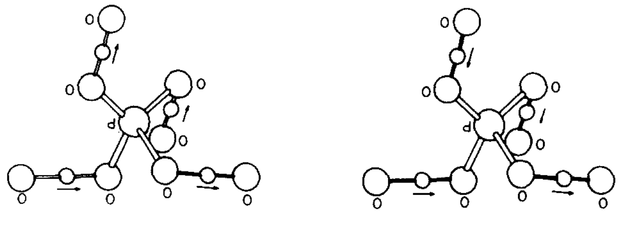

Fig. 1. Displacements of the oxygen atoms and the protons in the two possible E-modes of KH_2AsO_4; both have the same eigenfrequencies.

$$\omega_E^2(\mathbf{q}, T) = 4\Gamma^2[T + \gamma J(\mathbf{q})]/T \qquad (6)$$

where Γ is the proton tunneling integral, $J(\mathbf{q})$ is the proton–proton interaction, and $\gamma = (1/3)(2U_2/U_1 - 1)$, where U_1 and U_2 describe the interactions between nearest neighbor 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 in equation (4) arises from the vicinity of the Brillouin zone boundary (Bzb) at q_{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_{Bzb} in equation (5) and since $J(q)$ change sign at q_{Bzb} we obtain

$$V_{zz} = \frac{C_E T}{T - \gamma T_c}. \qquad (7)$$

We can determine γ from the experimental data for χ_x using the relation $\chi_x \propto (T + \gamma T_c)^{-1}$. The available susceptibilty data for CDA[6] and KDA[7] are shown in Fig. 2. Now, the contribution from q_{Bzb} alone already gives a value of γ 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 γ 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_B and C_E 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 $C_B \ll C_E$. It should also be noted that for KDA it is known experimentally[8] that $\chi_x(q = 0) > \chi_z(q = 0)$ in the major portion of the temperature range of interest here. Since $\chi_x(q)$ increases with increasing q [equations (5), (6)] while $\chi_z(q)$ decreases, χ_x should be even more dominant near the Bzb.

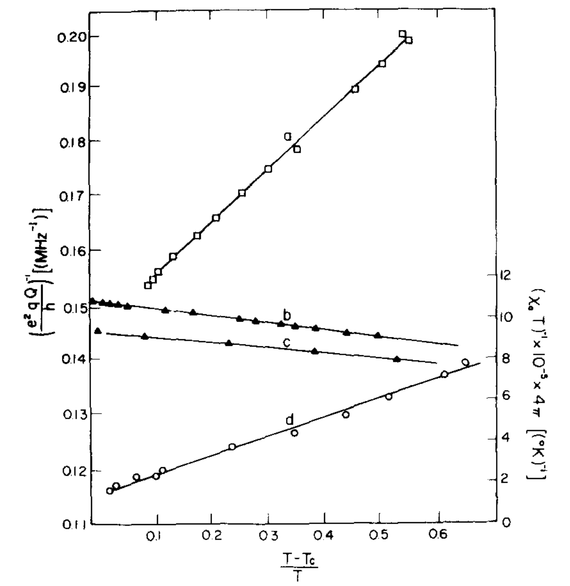

Fig. 2. Curves a and b describe V_{zz}^{-1} and $(\chi_a T)^{-1}$ for CsH_2AsO_4. The points refer to the experimental data.[1,6,7] The solid lines are the predictions of the theory, calculated from equation (4) and equation (5). Curves c and d describe the same quantities as above for KH_2AsO_4.

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-independence of V_{zz} measured at Cs site in CsH_2AsO_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 fluctuations. 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 α in equation (1), as seen from Table 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_{Bzb} to V_{zz}) from above T_c, to where it intersects the temperature axis. In this way one obtains for $\beta_c\Gamma < 1$

$$\alpha \approx \gamma - \tfrac{2}{3}(1 - \gamma)(\beta_c\Gamma)^2. \qquad (8)$$

However, since $\beta_c\Gamma$ decreases with deuteration and $\gamma < 1$, it follows that α 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 deutrons also increases the lattice constants, thus decreasing V_{zz}. This predicted behaviour of V_{zz} is indeed borne out by experiment.[1]

Acknowledgments – We wish to acknowledge many helpful discussions with Professor M. Klein. We also wish to express our thanks to Professor M. Luban for a critical reading of the manuscript and to Dr. E. Litov and H. Sompolinsky, for several valuable comments.

REFERENCES

1. BLINC R. & BJORKSTAM J.L., *Phys. Rev. Lett.* **23**, 788 (1969); BLINC R., MALI M., PIRS J. & ZUMER S., *J. Chem. Phys.* **58**, 2262 (1973).
2. SCOTT J.F. & WORLOCK J.M., *Solid State Commun.* **12**, 67 (1973).
3. HAVLIN S., LITOV E. & SOMPOLINSKY H., *Phys. Lett.* **53A**, 41 (1975).
4. KOBAYASHI K.K., *J. Phys. Soc. Japan,* **24**, 497 (1968).
5. BLINC R & MALI M., *Solid State Commun.* **7**, 1413 (1969).
6. POLLINA R.J. & GARLAND C.W., *Phys. Rev.* **B12**, 362 (1975).
7. BUSCH G., *Helv. Phys. Acta* **11**, 269 (1938); HAVLIN S., LITOV E. & UEHLING G.A., *Phys. Rev.* **B9**, 1024 (1974).
8. KAMINOW I.P., *Phys. Rev.* **138**, A1539 (1965).