Incommensurate phase in doped KH_2PO_4 from electron-spin-resonance measurements

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ESR measurements of KH_2PO_4 crystals doped with arsenic exhibit altered line shapes similar to those produced by an incommensurate phase. The modified line shapes occur in a range of temperatures extending approximately 17 K below the paraelectric-ferroelectric critical temperature T_c. The form and temperature dependence of the lines are in reasonable agreement with the predictions of the phase-soliton theory. The parameters h_1 and h_2 determining the variation of the resonant magnetic field show a power-law behavior as a function of temperature. The significance of the experimental results is discussed in the light of earlier studies which indicate a ferroelectric structure with four types of domains differing in electric polarization and in spatial orientation.

Experimental evidence in the form of altered electron-spin-resonance line shapes indicates strong distortion in crystals of KH_2PO_4 doped with arsenic in a temperature range extending from the ferroelectric transition temperature 123 K to approximately 106 K. The form and temperature dependence of the line shape in this range are consistent with the existence of an incommensurate phase. The data, in fact, agree with the predictions of the one-dimensional phase-soliton model, and the temperature dependence of the parameters is consistent both with theory and with observations in other ferreoelectric systems. There is, however, no direct evidence to indicate that an incommensurate phase exists in this material, and an alternative interpretation in terms of the distortions associated with domain walls will also be considered. Since no quantitative predictions following from this second interpretation are available, and since certain features discussed below make it problematical, we present a comparison of our results with the soliton model of an incommensurate phase even in the absence of corroborating evidence or a clear picture of the structure of such a phase.

A number of ferroelectric crystals[1] exhibit phases in which the ions of the lattice have a modulated displacement with a period that is incommensurate with the period of the lattice. Most of these are ferroelectrics of the displacive type, although a few[2] do not show a soft mode above the temperature T_I below which an incommensurate phase appears. These crystals become ferroelectric at a temperature T_c ($<T_I$) at which the periodicity of the modulated displacement, which is correlated with the electric polarization, "locks in" to a value commensurate with the lattice constant. In this paper, we present experimental evidence for the existence of distortions of the lattice similar to those produced by an incommensurate phase in a doped ferroelectric from a family of the order-disorder type. In the doped potassium dihydrogen phosphate (KDP) crystals examined in this experiment, the evidence indicates the onset of distortion at or near the ferroelectric-paraelectric critical temperature $T_c=123$ K. This distortion persists to a lower temperature of about 106 K, where the data indicate the normal line shape typical of an undeformed lattice.

The experimental data are obtained from measurements of the electron spin resonance (ESR) line shape as a function of temperature in crystals doped with arsenic. Although the most direct experimental evidence for the existence of incommensurate phases in other materials comes from x-ray and neutron scattering measurements,[3,4] where the periodicity of the modulations can be inferred directly from the data, ESR measurements provide strong evidence for the lattice deformation which accompanies an incommensurate modulation. When interpreted in terms of the one-dimensional phase-soliton model of the lattice distortion, the ESR line shape shows a sensitive and characteristic dependence[5-7] on the temperature through thermal variations of the phase $\phi(x)$ of the soliton. Both the spatial and the thermal dependence of the phase are determined by minimizing a phenomenological form of the free energy, which requires that $\phi(x)$ satisfy the sine-Gordon equation. The spatial variations in ϕ imply a modulated lattice distortion in which the arsenic impurities experience an inhomogeneous environment which can be characterized by a distribution of the field h at which resonance occurs. This distribution leads to a prediction of the line shape in the incommensurate region.

When crystals of KDP are doped with a small amount ($\sim 5\%$) of arsenic and irradiated with x-rays, the resulting free radical ions produce an ESR spectrum composed of four hyperfine lines arising from the As nuclear spin $\frac{3}{2}$. Earlier measurements[8,9] have shown that when a crystal with a particular orientation is cooled, each hyperfine line splits into two components at a temperature T^* well above the transition temperature T_c. In the present experiment, anisotropy of the g factor and of the hyperfine coupling constant prevents resolution of all but the lowest frequency doublet, for which T^* is approximately 250 K. The two components originate from regions of

different local electric polarization, parallel and antiparallel to the c axis, which persist for times greater than the inverse linewidth. On further cooling the lines become narrower and farther separated as the ferroelectric transition temperature $T_c = 123$ K is approached. Cooling below T_c produces no further separation.

Detailed observations of the line shape were made in a temperature range of 17 K extending from T_c to about 106 K. The observed line shapes are presented in the left column of Fig. 1 and corresponding theoretical curves of the phase-soliton model are shown in the right column. Note that the distortion in the line shape first appears as the crystal is cooled below 123 K, indicating that the ferroelectric critical temperature T_c in this material is experimentally indistinguishable from the temperature T_I at which the onset of incommensurability is taken to occur in the model. The resonant field h is assumed[5,6,10] to depend on the phase $\phi(x)$ through an expansion in the local displacement of the lattice at the point x, which is proportional to $\cos\phi(x)$:

$$h = h_0 + h_1\cos\phi(x) + \tfrac{1}{2}h_2\cos^2\phi(x) \ . \tag{1}$$

In the absence of solitons, the ions of the lattice are uniformly distributed, giving a probability density $dP/dx = c_1$, where c_1 is a constant. The distribution of the resonant field h is therefore given by

$$dP(h) = c_1\,dx = \frac{c_1\,dh}{|dh/dx|} = c_1\left|\frac{1}{(d\phi/dx)(h_1 + h_2\cos\phi)\sin\phi}\right| dh \ . \tag{2}$$

The form of $d\phi/dx$ is obtained from the first integral of the sine-Gordon equation:

$$\frac{d\phi}{dx} = c_2[\Delta^2 + \cos(\tfrac{1}{2}p\phi)]^{1/2} \ . \tag{3}$$

The integration constant Δ, which can be fixed in the theory by minimizing the free energy, is closely related to the soliton density n_s, generally defined as the ratio of the soliton width to the soliton spacing. The relation between the two quantities is

$$n_s = K\left[\frac{1}{\sqrt{1+\Delta^2}}\right] , \tag{4}$$

where $K(x)$ is the elliptic integral of the first kind. The integer p determines the number of values of the lattice displacement for which the free energy has a minimum, and thereby controls the structure of the commensurate phase to which the system "locks in" at low temperature. The distribution $dP(h)$ given by Eq. (2) is singular when $\sin\phi = 0$, and when $\cos\phi = -h_1/h_2$, giving characteristic peaks in the line shape. The line intensity profiles can be calculated by integrating $P(h)$ with an inhomogeneous line shape function $G(h)$ of Gaussian form and width σ:

$$I(h) = \int_0^\infty P(h')G(h - h')dh' \ . \tag{5}$$

The line intensities shown on the right-hand side of Fig. 1 were calculated from Eqs (1)–(5), and fitted to the experimental curves by varying h_1, h_2, and Δ, and visually comparing the plots. In the visual fits, the linewidth was taken to have the same value observed for the undistorted line above T_c. The shape of the curves was found to be sufficiently sensitive to small variations in the values of the field parameters h_1 and h_2 to give confidence in their determination as a function of temperature. Later the parameter values were checked at four temperatures by means of a fitting program which also allowed for variation of the linewidth. The values of h_1 and h_2 were only slightly affected, while the linewidth showed the expected slight decrease with temperature. The value of Δ could not be fixed as accurately by fitting the experimental data, but showed a general decrease as the temperature was lowered. The theoretical curves are insensitive to the value of p except at the lowest temperatures for which distortion was observed, where Δ was found to be small. A constant phase which can be added to ϕ in Eq. (1) was also varied, the best fit being obtained with the value zero.

The return to a nearly normal line shape at low temperatures appears to indicate a decrease in the deformation of the lattice, as indicated in Fig. 2. In the phase-

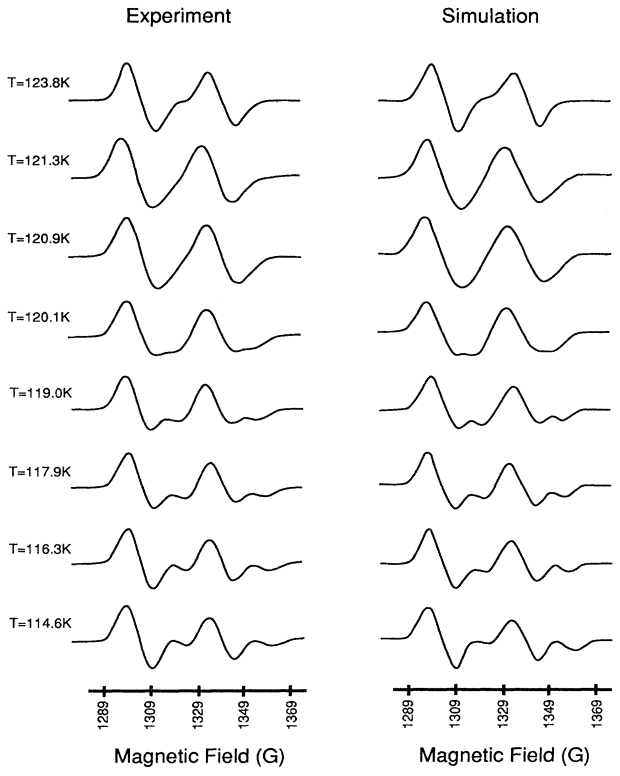

FIG. 1. Experimental and simulated line shapes. The derivative of the observed ESR line intensity of the lowest hyperfine line in the spectrum of As is plotted in the left-hand column as a function of the external magnetic field for temperatures ranging from just above the paraelectric-ferroelectric critical temperature $T_c \approx 123$ K to a few degrees below. The right-hand column shows shapes calculated from Eq. (5) at the same temperatures by adjusting the parameters h_1, h_2, and Δ.

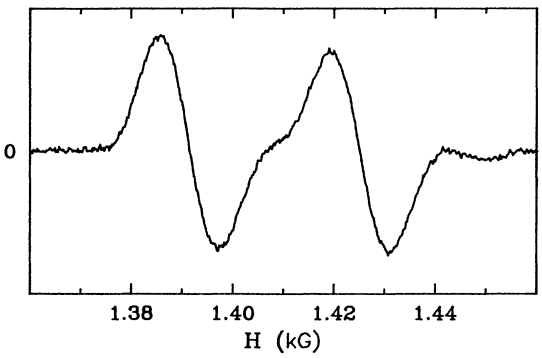

FIG. 2. Observed line shape at $T=106$ K. Little distortion is evident, the shape being very close to that observed for $T>123$ K.

soliton theory, this would correspond to a transition to commensurability. It is not possible to fix the temperature at which this occurs with precision because of the gradual nature of the transition.

Figure 3 shows a plot of $\ln h_1$ and $\ln h_2$ versus the logarithm of the dimensionless temperature variable $t=(T_I-T)/T_I$ where T_I is the temperature at which the incommensurate phase appears as the crystal is cooled, taken to be identical with the paraelectric-ferroelectric critical temperature T_c. The linear variation indicates a power-law behavior of h_1 and h_2 with t:

$$h_1=a_1t^{\beta}, \qquad h_2=a_2t^{2\beta}. \tag{6}$$

The exponents β and 2β are determined independently from the measured slopes to have the values 0.33 and 0.65, respectively. The accuracy of this determination can be assessed by noting that the estimated error in determining h_1 and h_2 from the fit is 5%. Figure 4 is a linear rather than a logarithmic plot of the same data indicating that h_1^3 and $h_2^{3/2}$ depend linearly on $T-T_I$. The same power-law behavior was noted by other authors[11] for displacive ferroelectrics.

Early x-ray[12,13] and neutron diffraction[14] studies of the paraelectric-ferroelectric transition in KDP and in the deuterated form KD_2PO_4 (DKDP) revealed the existence of four types of domains in polarized crystals below the critical temperature T_c. The change from tetragonal to orthorhombic symmetry that occurs at T_c is accompanied by a distortion of the PO_4 tetrahedra, resulting in a shear in which the cell is stretched along the [110] or [$\bar{1}$10] direction of the original paraelectric tetragonal cell. The sense of the displacement of P and K ions parallel to the c axis, and therefore also the direction of electric polarization, is correlated with the general direction of this shear. Within a domain of given polarization, there are two stable orientations of the sheared cell relative to the axes of the tetragonal cell. The new axes can be aligned either along the [100] direction or along the [010] direction. The existence of cells aligned along the [110] is also reported in Ref. 13, apparently as a transitional orientation within the wall between domains of different polarization. The considerable elastic stresses resulting from the different shear axes and different orientations do not result in a formation of microcrystals, as shown by the fact that, despite some hysteresis, a multidomain structure reappears upon application of a depolarizing field after an applied field has produced complete single-domain polarization. The stresses occur in the neighborhood of domain walls both within and between regions of the same polarization.

A suggested pattern of domain walls, following observations and diagrams given in Refs. 12–14, is shown in Fig. 5. Note the existence of four types of domain, two of positive polarization stretched along an approximate [110] direction, and differing slightly in orientation, and two of negative polarization stretched along an approximate [$\bar{1}$10] direction, and also differing in orientation.

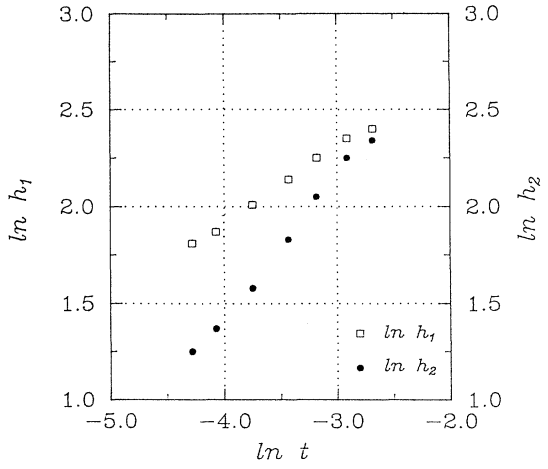

FIG. 3. Variation of parameters with temperature. Logarithms of the parameters h_1 and h_2 are plotted as functions of the logarithm of the reduced temperature $t=(T_I-T)/T_I$, showing evidence for a power-law dependence.

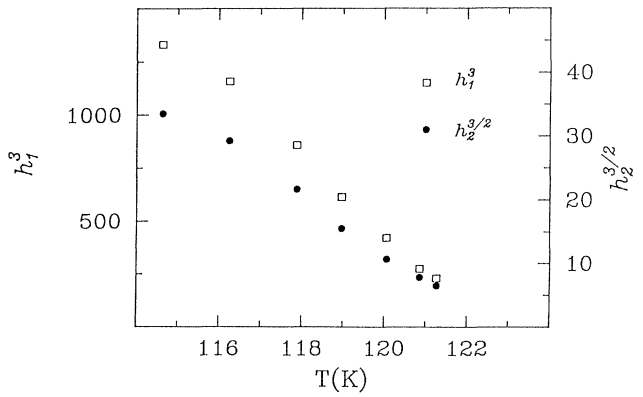

FIG. 4. Variation of parameters with temperature. The third power of h_1 and the $\frac{3}{2}$ power of h_2 are plotted as functions of the temperature T.

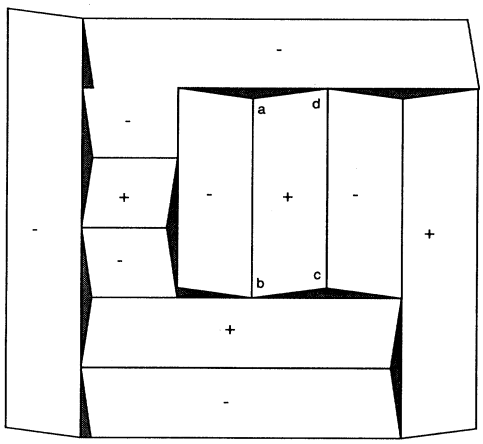

FIG. 5. Possible pattern of domain walls in the ferroelectric phase of KDP. There are two types of boundary between domains: (i) a twinning interface (*ab* or *cd*) between domains of positive and negative polarization, and (ii) walls (*bc* or *da*) between regions in which the crystal planes nearly parallel to the wall have a slightly different spatial orientation. Walls of the second type can occur either within a region of given polarization (*bc*) or as part of the boundary between positive and negative regions (*da*).

The presence of domains of both polarizations is primarily due to the dipolar interaction, while the correlation between the shear direction and the direction of polarization is inherent in the mechanism that is responsible for the ferroelectric phase transition. Fitting together of these four types of domain results in two distinct types of domain wall. One type, designated *ab* or *cd* in the figure, is simply a twinning plane dividing a region of positive and a region of negative polarization. This is presumably a very thin wall with very little associated elastic strain. The other type is represented by *bc* or *da* in the figure. This type of wall, which can occur either within a region of given polarization (*bc*) or as part of the boundary between positive and negative regions (*da*), is clearly associated with great elastic stress, since voids would be present in the crystal if this were not the case. In view of the quasireversible nature of the structure, it is reasonable to assume that the spacing between twinning planes is determined by a competitive interplay between terms in the free energy associated with the dipolar interaction, the elastic interaction, and the barrier between the twinned states.

The existence of this domain structure and the success of the soliton theory in accounting for the shape of the ESR lines over a range of temperatures raises questions concerning the correct interpretation of the experimental results presented here. It seems unlikely that elastic strains associated with the domain walls would result in the modification and temperature dependence of the ESR line shape predicted by the soliton theory. The reappearence of a nearly normal line shape only a few degrees below the transition temperature is difficult to reconcile with this picture, since the lattice strains may be expected to persist as long as the crystal structure is orthorhombic. The fact that these lattice distortions do not markedly alter the line shape at the lowest temperatures observed must be explained in any theoretical account of the results. The presence of an incommensurate phase, on the other hand, is not supported by any direct thermodynamic or structural evidence, although it probably cannot be ruled out, particularly in the case of the doped crystal. The pattern of phases as a function of temperature is different in our case from that observed in most ferroelectrics, where incommensurability occurs above the paraelectric-ferroelectric transition temperature T_c, an exception being the displacive ferroelectric barium sodium niobate ($Ba_2NaNb_5O_{15}$), which has a ferroelastic transition[15] below T_c leading to an incommensurate phase which persists for about 30 K, so that incommensurability coexists with spontaneous ferroelectric polarization. Finally, we have no crystallographic picture of the structure of a hypothetical incommensurate phase in doped KDP, and we are not aware of any study that suggests the possible nature of such a phase. An interesting possibility is that the factors cited at the end of the last paragraph might lead to a one-dimensional incommensurate-like structure associated with the domain walls, and leading to regular, possibly temperature-dependent, spacing of the twinning interfaces which could mimic the results of the soliton theory.

The specific structure of the domain walls cited in this paper might be the key to the understanding not only of our present results, but also of other interesting features of this family of ferroelectrics, such as the dynamics of domain-wall motion. Further theoretical study of this structure would be desirable.

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