82891-29-0; didehydro-**12** sulfoxide, 82891-33-6; **13** (α-OAc), 82891-24-5; **13** (β-OAc), 82891-25-6; **14** (α-OAc), 81470-13-5; **14** (β-OAc), 82891-26-7; **15** (α-OAc), 81470-14-6; **15** (β-OAc), 81470-18-0; **16** (α-OAc), 81470-16-8; **16**, 81470-19-1; 2-methyl-1,3-cyclohexanedione, 1193-55-1; 2-methyl-1,3-cyclopentanedione, 765-69-5; ethyl 2-oxocyclopentanecarboxylate, 611-10-9; 2-oxocyclohexanecarbonitrile, 4513-77-3; methyl 2-methyl-3-oxopropanoate, 51673-64-4; 5aβ-methyl-6β-benzoyloxy-3-phenylsulfoxide 2,4,5,5a,6,7,8,9-octahydro-2-naphtho[1,2-*b*]furanone, 82891-31-4.

Supplementary Material Available: Spectroscopic data for compounds **3** and **8–16** (2 pages). Ordering information is given on any current masterhead page.

Electron Paramagnetic Resonance Detection of Electric Field Effect on the Nucleation of the Ferroelectric Phase of KD_2PO_4

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Received May 3, 1982

We report here, to our knowledge, the first study by electron paramagnetic resonance (EPR) spectroscopy of the growth of one structural phase into another and the feasibility of influencing the nucleation kinetics of not only a phase but also a domain with a certain polarization. The paraelectric–ferroelectric phase transition[1] of KD_2PO_4 at $T_c = 221$ K was chosen as an example, and the growth rate of the ferroelectric phase was investigated as a function of temperature and externally applied electric field.

KD_2PO_4 was chosen since it is a typical member of a family of hydrogen-bonded compounds whose paraelectric–ferroelectric phase-transition mechanism is not fully understood,[1] and its ferroelectric property made it possible to influence the structural ordering via easily accessible electric fields. The deuteration was employed because the smaller hyperfine splittings from deuterons (as compared to protons) result in simpler EPR spectra. For this reason, KD_2PO_4 was prepared from a vacuum line synthesis from K_2CO_3, P_2O_5, and D_2O. The value of T_c (221 K), determined[2] via microwave dielectric loss at 9.4×10^9 Hz, indicated that the deuteration level was ~99%.[1]

Since KD_2PO_4 is diamagnetic, the EPR studies were carried out on samples into which SeO_4^{3-} radicals were introduced by γ irradiation of KD_2PO_4 crystals doped with ~1 mol % of K_2SeO_4, as described earlier.[3-6] The SeO_4^{3-} probe was preferred over AsO_4^{4-} and CrO_4^{3-}, the other two paramagnetic probes which have been widely used[7] for studying ferroelectric transitions, since SeO_4^{3-} has the same electric charge and site symmetry as a PO_4^{3-} unit in the original lattice, as has been shown by detailed ENDOR (electron nuclear double resonance) measurements.[5] The AsO_4^{4-} probe, formed by doping KD_2PO_4 with ~5% KD_2AsO_4 and γ irradiation,[5,7] has an extra negative charge compared to the substituted (PO_4^{3-}) unit. This excess charge alters local electric field gradients and hence modifies the local ionic displacements near T_c. Similarly detailed ENDOR measurements have shown[8] that the site symmetry of CrO_4^{3-} is distinctly lower (C_s) than that (D_{2d}) of PO_4^{3-} in KH_2PO_4.

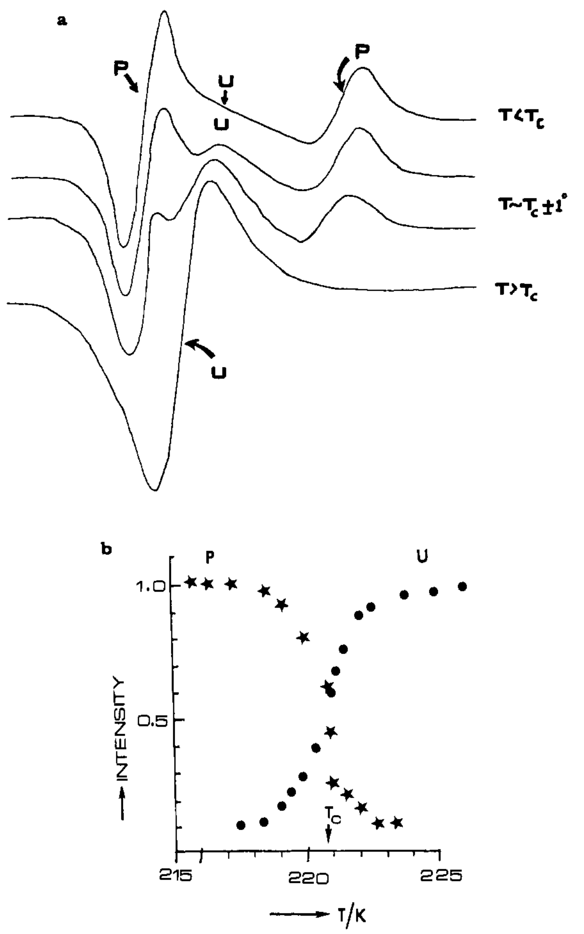

Figure 1. (a) Temperature dependence of the low-field ^{77}Se hyperfine component of the SeO_4^{3-} radical in KD_2PO_4 near $T_c = 221$ K. The signals labeled U and P refer to those from the "unpolarized" and the "polarized" regions. (b) Temperature dependence of the intensity of the P and the U signals, reflecting the growth of the polarized regions in the paraelectric sample in the vicinity of T_c.

The D_{2d} symmetry of SeO_4^{3-} in KD_2PO_4 was verified by analyzing the angular dependence of its EPR spectrum in terms of the electron Zeeman tensor (**g**) and the hyperfine tensor (**A**) with a numerical diagonalization procedure.[5] The results for the ferroelectric phase are as follows:[5b] $g_{xx} = 2.002 \pm 0.005$, $g_{yy} = 2.001 \pm 0.005$, $g_{zz} = 2.001 \pm 0.003$; $A_{xx} = 2988 \pm 8$ MHz, $A_{yy} = 3138 \pm 8$ MHz, $A_{zz} = 3486 \pm 6$ MHz. Here the z direction coincides with the c axis and the x axis is oriented at 30 ± 2° with respect to the a axis of the tetragonal crystal abc system. These results are essentially identical with those for KH_2PO_4,[5,9] where this probe was identified via ENDOR, thus confirming its formation in KD_2PO_4.

Spectral changes relevant to the nucleation phenomenon are observed within 5 K of T_c. Figure 1a shows the temperature dependence of the low-field component of the ^{77}Se hyperfine line labeled U (for "unpolarized"). At $T = T_c + 3$, the signal is a singlet exhibiting axial symmetry on crystal rotation about the c axis, conforming with the tetragonal symmetry of the paraelectric phase of KD_2PO_4. On approaching T_c (from $T > T_c$), this signal is seen to be flanked by two sharper signals, labeled P (for "polarized"). As the temperature is lowered further the P signals increase in intensity at the expense of the U signals and at ~2.5

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(1) Lines, M.; Glass, A. M. "Principles and Applications of Ferroelectrics and Related Materials"; Clarendon Press, Oxford, 1977.

(2) The experimental procedure for determining T_c via microwave dielectric loss measurements was similar to that described by Gough et al. (Gough, S. R.; Ripmeester, J. A.; Dalal, N. S.; Reddoch, A. H. *J. Phys. Chem.* **1979**, *83*, 664). A temperature hysteresis of 1.5 K (maximum) was noted. Temperature was controlled to within 0.5 K and measured with a copper–constantan thermocouple. The temperature gradient across the sample was less than 0.5 K, as judged by the EPR and T_c measurements on samples of widely different sizes.

(3) Hukuda, K. *J. Phys. Soc. Jpn.* **1975**, *38*, 150. Hukuda, K.; Nakagawa, Y. *Ibid.* **1978**, *44*, 1588.

(4) Kawano, T. *J. Phys. Soc. Jpn.* **1974**, *37*, 848.

(5) (a) Dalal, N. S.; Hebden, J. A.; Kennedy, D. E.; McDowell, C. A. *J. Chem. Phys.* **1977**, *66*, 4425. (b) Due to a printing error in 5a, the parameters for $KD_2PO_4{:}SeO_4^{3-}$ for $T < T_c$ were incorrect. The present work corrects this error.

(6) Dalal, N. S. *Ferroelectrics* **1981**, *39*, 1060.

(7) (a) Adriaenssens, G. J. *J. Magn. Reson.* **1977**, *25*, 511. (b) Dalal, N. S. *Adv. Magn. Reson.*, in press.

(8) Gaillard, J.; Gloux, P.; Muller, K. A. *Phys. Rev. Lett.* **1977**, *38*, 1216.

(9) The corresponding values for SeO_4^{3-} in KH_2PO_4 are as follows: $g_x = 1.9997$, $g_y = 2.0158$, $g_z = 2.0036$; $A_x = 2986$ MHz, $A_y = 3055$ MHz, $A_z = 3490$ MHz. For details see ref 5.

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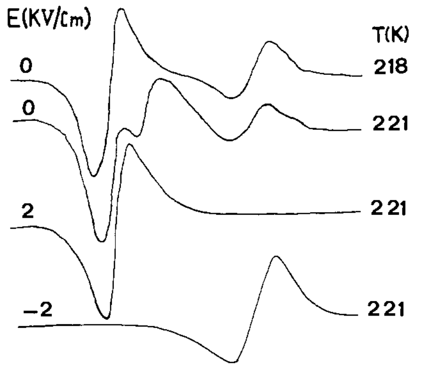

Figure 2. Electrid field effect on the "polarized" (P) and "unpolarized" (U) portions of a KD_2PO_4 sample near T_c.

± 0.5 K below T_c, only the P signals persist, with no further significant change down to 77 K. Earlier studies[3-6,13] in the ferroelectric phase have shown that these two P-type signals represent the two possible (positively and negatively charged) domains of electric polarization below T_c. Figure 1b shows the temperature variation of the intensity of the P and the U signals. The rather rapid variation observed suggests that it is related to the cooperative ordering near T_c.

That the P signals are detected about 3 K *above* T_c, that their intensity increases rapidly as $T \rightarrow T_c$, and that these are the only signals well below T_c imply the following picture as the lattice approaches T_c: As $T \rightarrow T_c$ (from $T > T_c$), the paraelectric phase lattice starts to grow small "islands" in which the local symmetry corresponds to that of the ferroelectric phase. These "ferroelectric phase islands" then grow in size as $T \approx T_c$, and finally at $T < T_c - 3$, these "islands" cover the complete lattice, which is then fully polarized. It must be mentioned that such predictions have been made recently via molecular dynamic computer simulations.[10] Evidence for such behavior was shown in an earlier NQR study on KH_2AsO_4,[11,12] but of course, the corresponding studies cannot be carried out on the phosphates because of the zero quadrupole moment of ^{31}P.

To verify that the P signals are related to "long-range" ordering regions and not simply to the freezing of some molecular motion on the EPR time scale, we studied the effect of an externally applied electric field.[13] The basis of this experiment was that while an electric field of only small (~2–3 kV/cm) intensity could "polarize" the crystal by reorienting all molecules into a single ferroelectric domain,[13] orders of magnitude higher electric fields would be needed to reorient an isolated molecule.[1,13] Since the polar axis of KD_2PO_4 is along *c*, electric fields of intensity *E* up to ±5 kV/cm were applied along this direction.[11] As shown in Figure 2, $E \sim 2$ kV/cm was sufficent to polarize the unpolarized part of the sample, since the U signal also changes into the remaining P signal. By reducing *E* it was possible to control the ratio of the polarized to the unpolarized portions and hence influence and observe the rate of growth of these long-range clusters. Similar electric field effects have been previously reported for the ^{75}As NMR spectrum in KH_2AsO_4.[11,12]

The electric field effect not only provides a strong support for the molecular dynamics (i.e., cluster) model of structural phase transitions but also provides a measure of the energy difference between the molecules in the paraelectric and ferroelectric phases near T_c (~2 kV/cm was the field necessary to polarize the whole crystal). Moreover, from the widths and separation of the two P components at $T \ll T_c$ we estimate that a molecule in a typical cluster has a lifetime of $\geq 10^{-8}$ s at 2 K above T_c. Furthermore, the detection of the coexistence of the two phases around T_c suggests that the transition in KD_2PO_4 is of the first order. The generally made statement[1] for the KD_2PO_4 transition is that it is second order but close to being first order (see, however, ref 14).

Another important conclusion is that for studying the lattice fluctuations near T_c of the KH_2PO_4-type compounds via EPR, the electronic charge and site symmetry of the paramagnetic probe must match those of the substituted group in the host, since earlier studies[5,7] of KD_2PO_4 using AsO_4^{4-} and CrO_4^{3-} probes (which, as mentioned here earlier, do not match the PO_4^{3-} units) did not detect changes near T_c such as detected here with SeO_4^{3-}. This conclusion can be verified by similar studies on KD_2AsO_4 and the many other members of this family.[1] Another critical experiment would be to study the antiferroelectrics $ND_4D_2PO_4$, $ND_4D_2AsO_4$, and their undeuterated analogues. We predict that such clusters would be observed via CrO_4^{3-}, but not by using SeO_4^{3-} or AsO_4^{4-}, since ENDOR studies[5,8] have shown that, of these three, only CrO_4^{3-} meets the charge and symmetry requirements for antiferroelectric lattices. We believe that the results reported here bear on some important and novel features of critical fluctuations and should stimulate further experimental ahd theoretical work on the microscopic picture of cooperative phenomena.

Acknowledgment. This research was supported in part by grants from the Research Corp., National Science Foundation, and the Energy Research Center of West Virginia University.

Registry No. KD_2PO_4, 13761-79-0; SeO_4^{3-}, 35473-43-9.

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(10) See, for example: Schneider, T.; Stoll, E. *Phys. Rev. Lett.* **1978**, *41*, 964. Ogita, N.; Veda, A.; Matsubara, T.; Matsuda, H.; Yonezawa, F. *J. Phys. Soc. Jpn., Supp.* **1969**, *26*, 145.

(11) Blinc, R.; Bjorkstam, J. L. *Phys. Rev. Lett.* **1969**, *23*, 788.

(12) Bjorkstam, J. L. *Adv. Mag. Reson.* **1974**, *7*, 1.

(13) For an experimental procedure for applying electric field and its manifestation in the EPR spectra of paramagnetic probes in ferroelectric crystals, see: (a) Dalal, N. S.; McDowell, C. A.; Srinivasan, R. *Phys. Rev. Lett.* **1970**, *25*, 823. (b) Truesdale, R. D.; Poole, C. P., Jr., Farrach, F. A. *Phys. Rev.: Condens. Matter* **1982**, *25*, 474 and references therein.

(14) It was pointed out by a referee that because of the very different masses of P and Se the EPR spectra may not reflect the true long-range order of the undoped lattice. This is true for impurities in general, so all impurity results must be cautiously interpreted. In the present case the temperature dependence of the EPR intensity of the P signals parallels that of high (microwave) frequency dielectric constant. Since the SeO_4^{3-} concentration is low (≤1%), the dielectric constant should reflect the behavior of the bulk of the crystal. On this basis it is felt that the SeO_4^{3-} probe senses the lattice ordering perhaps fairly faithfully. We thank the referee for highlighting this point, which we plan to discuss in detail in a forthcoming publication.

Carbon-14 Isotope Effects in the Addition of 2,4-Dinitrobenzenesulfenyl Chloride to Styrene-*1*-^{14}C and Styrene-*2*-^{14}C

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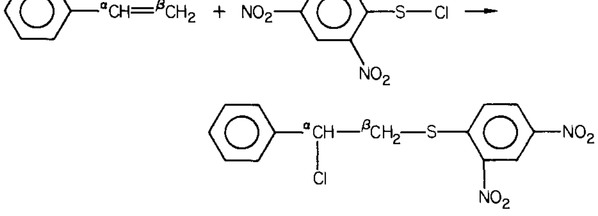
Received May 12, 1982

As the first reported example of a carbon isotope effect in a simple electrophilic addition reaction, we have found that there are substantial kinetic isotope effects in the addition of 2,4-dinitrobenzenesulfenyl chloride to both α (styrene-*1*-^{14}C) and β (styrene-*2*-^{14}C) carbon-14 labeled styrenes (eq 1–3).



(1)

$$^{12}k/^{14}k \text{ for } ^{\alpha}C = 1.022 \pm 0.0034 \qquad (2)$$