

ventional magnetic transitions, where  $\beta$  (three-dimensional)  $< \beta$  (mean-field).

We should note that our results do not agree with the calculation of  $\beta$  by Harris, Lubensky, and Chen.<sup>17</sup> By expanding about six spatial dimensions they obtain

$$\beta(d) \sim 1 + (6 - d)/2 \quad (6)$$

for dimension  $d$  less than 6. The disagreement may mean only that six spatial dimensions is too far from the real world for the analytic continuation to be valid.

Further study of static and transport<sup>18</sup> properties of spin-glasses like the present films will be valuable. When the critical temperature is sufficiently high that no "glassy" phenomena (i.e., slow relaxation and hysteresis) occur in the critical region, the susceptibility cusp can be clearly resolved. The importance of doing such measurements in the lowest possible external fields should be apparent from Figs. 1 and 2.

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### <sup>31</sup>P Chemical-Shift Study of the Ferroelectric Transition in KD<sub>2</sub>PO<sub>4</sub>

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The <sup>31</sup>P chemical-shift tensors  $\vec{\sigma}$  have been determined as a function of temperature on going through the ferroelectric phase transition in a single crystal of KD<sub>2</sub>PO<sub>4</sub>, and an abrupt change in  $\vec{\sigma}$  was found at  $T_c$ . The results show that the transition is not driven by an electronic instability but is a pure lattice transition of the order-disorder type, and demonstrate the usefulness of chemical-shift studies of structural phase transitions in solids.

In this paper we report what we believe to be the first study of a ferroelectric phase transition via the determination of a chemical shift tensor. With the help of a superconducting magnet and a pulsed NMR spectrometer we have determined the temperature dependence of the <sup>31</sup>P chemical-shift tensor in a single crystal of KD<sub>2</sub>PO<sub>4</sub> on going through the ferroelectric phase transition at  $T_c = 220^\circ\text{K}$ . The results show that this ferroelectric transition is not driven by an electronic instability<sup>1</sup> but is a pure lattice transition of the

order-disorder type, and demonstrate the usefulness of chemical shift studies of structural phase transitions in solids.

Chemical shifts in solids are usually masked by much stronger nuclear magnetic dipolar interactions and until recently this technique could not be used for the study of structural phase transitions. In the usual NMR spin Hamiltonian

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_O + \mathcal{H}_d, \quad (1)$$

the dipolar term  $\mathcal{H}_d$  is smaller than the Zeeman

term  $\mathcal{H}_z$  but significantly larger than the chemical-shift term  $\mathcal{H}_0$ :

$$\mathcal{H}_0 = \gamma \sum_i \vec{I}_i \cdot \vec{\sigma}_i \cdot \vec{H}_0 \ll \mathcal{H}_d. \quad (2)$$

Two developments have changed this situation. Waugh, Huber, and Haeberlen<sup>2</sup> have developed multipulse NMR techniques which allow the measurement of chemical shifts in solids by averaging out the spin part of the truncated dipolar Hamiltonian  $\mathcal{H}_d'$ . A less general method—made possible by the development of superconducting magnets of high homogeneity—is to go to higher magnetic fields, thereby increasing  $\mathcal{H}_z$  and  $\mathcal{H}_0$  while keeping  $\mathcal{H}_d$  constant. It was this last approach combined with isotopic dilution (i.e., deuteration) to reduce the heteronuclear  $\mathcal{H}_d$  which we used in the present study. The <sup>31</sup>P Larmor frequency  $\gamma_L = \omega_L/2\pi$  was 97 MHz and the chemical shifts were much larger than the dipolar width of the <sup>31</sup>P line. The shifts were measured relative to an 85% H<sub>3</sub>PO<sub>4</sub> solution and no corrections were made for the difference in the magnetic susceptibilities between the sample and the standard. The experimental error in the chemical shifts is about 10%.

There are four <sup>31</sup>P nuclei per unit cell of KH<sub>2</sub>PO<sub>4</sub> both above and below  $T_c$ .<sup>3</sup> In the paraelectric phase the <sup>31</sup>P nuclei sit at the centers of the PO<sub>4</sub> tetrahedra which are linked by O-H- -O hydrogen bonds to form a three-dimensional lattice.<sup>3</sup> The edges of two PO<sub>4</sub> tetrahedra are rotated by +13° (*A* sites) with respect to the orthorhombic crystal *a, b* axes, whereas the other two are rotated by -13° (*B* sites) with respect to the same axes. At  $T = 22^\circ\text{C} > T_c$  all phosphorus sites were found to be chemically and physically equivalent. From the angular rotation patterns (Fig. 1), we determined the <sup>31</sup>P chemical-shift tensor in the crystal fixed *a, b, c* coordinate system as

$$\vec{\sigma}(\text{ppm}) = \begin{pmatrix} 12 & 0 & 0 \\ 0 & 12 & 0 \\ 0 & 0 & -15 \end{pmatrix}, \quad T > T_c. \quad (3)$$

$$\vec{\sigma}_{1,4}(\text{ppm}) = \begin{pmatrix} 30 & \mp 52 & 0 \\ \mp 52 & -15 & 0 \\ 0 & 0 & -15 \end{pmatrix}, \quad \vec{\sigma}_{2,3}(\text{ppm}) = \begin{pmatrix} -15 & \pm 52 & 0 \\ \pm 52 & 39 & 0 \\ 0 & 0 & -15 \end{pmatrix}, \quad T < T_c. \quad (4)$$

These results differ from those of Ref. 4, where—because of the method used—only one average  $\vec{\sigma}$  tensor could be obtained<sup>4</sup> below  $T_c$ .

The above tensors reflect the reduced crystal symmetry— $C_{2v}^{19}(mm2)$ —in the ferroelectric phase. The <sup>31</sup>P nuclei lie now on a twofold axis which is parallel to the crystal *c* axis. The nuclei are shifted by 0.08 Å from the center of the PO<sub>4</sub> tetrahedra along the ferroelectric (*c*) axis.<sup>3</sup> With the help of symmetry arguments we can immediately assign  $\sigma_1$  to the *A* sites and  $\sigma_3$  to the *B* sites of a given ferroelec-

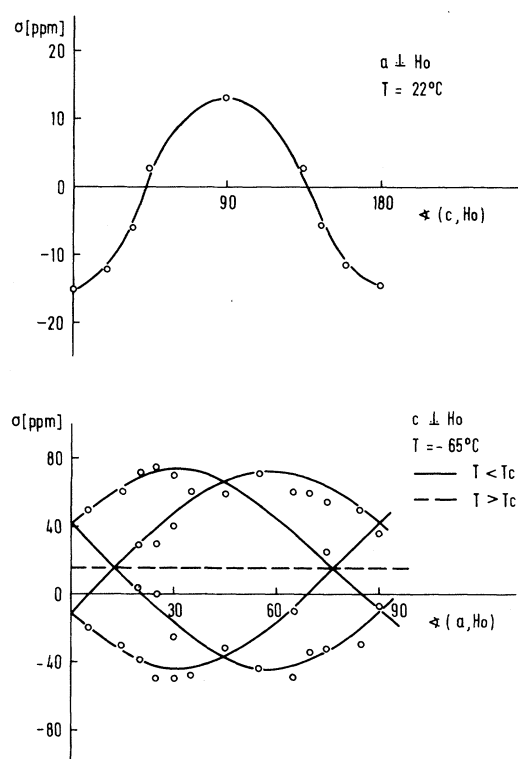


FIG. 1. Angular dependence of the <sup>31</sup>P chemical shift relative to 85% H<sub>3</sub>PO<sub>4</sub> in a single crystal of KD<sub>2</sub>PO<sub>4</sub> at  $T = 22^\circ\text{C}$  and at  $-65^\circ\text{C}$ .

The <sup>31</sup>P chemical-shift tensor is—as required by the crystal symmetry<sup>3</sup>  $D_{2d}^{12}(42m)$ —axially symmetric around the fourfold *c* axis which passes through the phosphorus sites.<sup>4</sup> The anisotropy  $\Delta\sigma = \sigma_{11} - \sigma_{33} = -27$  ppm is rather small. The chemical-shift tensor depends only little on temperature in the paraelectric phase but changes abruptly at  $T_c$  on going into the ferroelectric phase, where it is again very nearly independent of temperature (Fig. 2).

14° below  $T_c$  at  $T = -65^\circ\text{C}$  we found (Fig. 1) four physically nonequivalent <sup>31</sup>P chemical-shift tensors, which are—in the crystal fixed *a, b, c* coordinate system—equal to

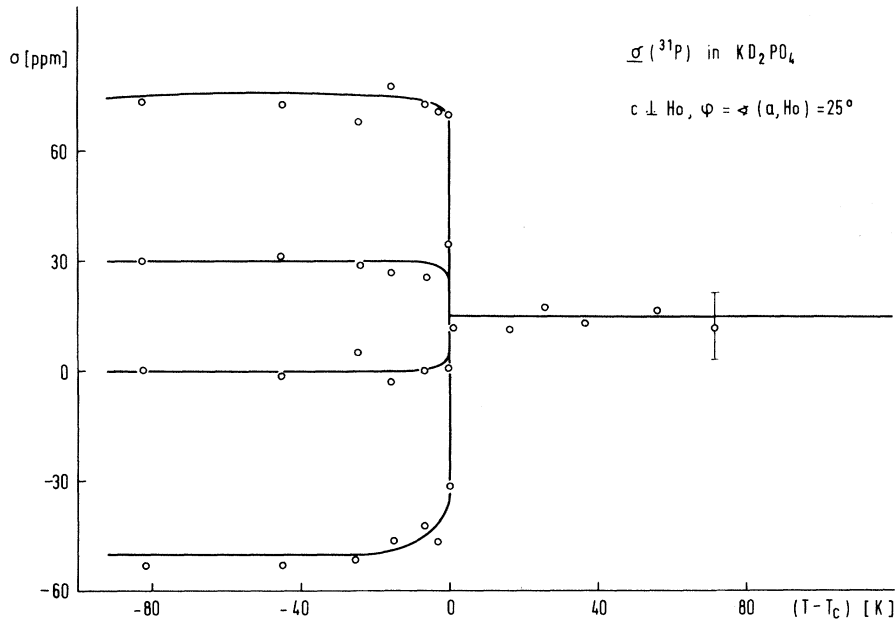


FIG. 2. Temperature dependence of the  $^{31}\text{P}$  chemical shift on going through the ferroelectric transition in  $\text{KD}_2\text{PO}_4$ .

tric domain, whereas  $\sigma_2$  and  $\sigma_4$  are the corresponding tensors for a domain where the direction of the spontaneous polarization is reversed by  $180^\circ$ :  $\sigma_1 = \sigma_A(+\vec{P})$ ,  $\sigma_2 = \sigma_A(-\vec{P})$ ,  $\sigma_3 = \sigma_B(+\vec{P})$ ,  $\sigma_4 = \sigma_B(-\vec{P})$ . All four tensors have the same eigenvalues:  $\sigma_{33} = 70$  ppm,  $\sigma_{22} = -46$  ppm,  $\sigma_{11} = -15$  ppm, but differ in the orientation of the principal axes. These are listed in Table I.

Though the crystal  $c$  axis is still a principal axis, the above tensors are no longer axially symmetric. The anisotropy  $\Delta\sigma = \sigma_{33} - \frac{1}{2}(\sigma_{11} + \sigma_{22}) = 100$  ppm is much larger than in the paraelectric phase. The asymmetry  $\eta = (\sigma_{11} - \sigma_{22})/(\sigma_{33} - \bar{\sigma})$ , which was zero in the paraelectric phase, now equals  $\eta = 0.46$ . The isotropic chemical shift  $\bar{\sigma} = \frac{1}{3}\text{Tr}\bar{\sigma} = 3$  ppm is, however, the same in the paraelectric as in the ferroelectric phase. This could not be the case if the phase transition were driven by electronic instabilities<sup>1</sup> and if as the

result of vibronic interactions a coupled electron-lattice branch of the spectrum of elementary excitations became unstable<sup>1,6</sup> at  $T_c$ . The ferroelectric transition in  $\text{KD}_2\text{PO}_4$  is thus a pure structural transition where the Born-Oppenheimer approximation is valid. Chemical-shift measurements thus allow a discrimination between "pure" structural transitions and "mixed" transitions,<sup>1,6</sup> where electron-lattice interactions are dominant as in Jahn-Teller<sup>6</sup> or metal-insulator transitions.

The above conclusion is supported by the fact that the paraelectric  $^{31}\text{P}$  chemical-shift tensor is just the average of the four "ferroelectric" ones (Table I) as expected for the case of deuteron ordering<sup>7</sup> coupled with a shift of the phosphorous atom. The present results thus represent further direct evidence for the coupled deuteron-lattice ion pseudospin soft-mode-type order-dis-

TABLE I. Direction cosines of the principal axes of the  $^{31}\text{P}$  chemical-shift tensors in ferroelectric  $\text{KD}_2\text{PO}_4$  at  $T = -65^\circ\text{C}$  ( $\sigma_{33} = 70$ ,  $\sigma_{22} = -46$ ,  $\sigma_{11} = -15$  ppm) with respect to the crystal  $a$ ,  $b$ ,  $c$  axes.

	$\vec{\sigma}_A(\vec{P})$			$\vec{\sigma}_A(-\vec{P})$			$\vec{\sigma}_B(\vec{P})$			$\vec{\sigma}_B(-\vec{P})$		
	$\sigma_{33}$	$\sigma_{22}$	$\sigma_{11}$	$\sigma_{33}$	$\sigma_{22}$	$\sigma_{11}$	$\sigma_{33}$	$\sigma_{22}$	$\sigma_{11}$	$\sigma_{33}$	$\sigma_{22}$	$\sigma_{11}$
$\cos\alpha$	0.86	-0.51	0	-0.51	0.86	0	0.51	-0.86	0	0.86	0.51	0
$\cos\beta$	0.51	0.86	0	0.86	0.51	0	0.86	0.51	0	-0.51	0.86	0
$\cos\gamma$	0	0	1	0	0	1	0	0	1	0	0	1

order nature of the ferroelectric transition<sup>7</sup> in  $\text{KD}_2\text{PO}_4$ .

It should be noted that the largest principal axis of the  $^{31}\text{P}$  chemical-shift tensor is nearly exactly parallel to the line connecting the two  $\text{PO}_4$  oxygens to which the deuterons are directly attached. A change in the  $\text{H}_2\text{PO}_4$  deuteron attachment from the "top" to the "bottom" oxygens—as viewed along the  $c$  axis—coupled with a corresponding shift of the P ions results in polarization reversal ( $\vec{P} \rightarrow -\vec{P}$ ) and a rotation of the two largest principal axes of the  $^{31}\text{P}$  tensor by  $90^\circ$  (Table I). The orientation of the principal axes of the  $^{31}\text{P}$  chemical-shift tensors is therefore a very sensitive indicator of the hydrogen arrangement and short-range order fluctuations in  $\text{KH}_2\text{PO}_4$ -type crystals.

Chemical-shift measurements in solids can thus provide valuable structural information in addition to solving the question whether a particular structural phase transition is electronically

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## Charge-Density-Wave Band Structure and Infrared and Visible Thermoreflectance of $2H\text{-TaSe}_2$

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We have measured the infrared and visible thermoreflectance of  $2H\text{-TaSe}_2$  in the charge-density-wave onset temperature range. New features that appear in the spectrum are compared with a model two-dimensional  $3 \times 3$  charge-density-wave calculation. We stress connection between the infrared result and the multiplet of transitions inside the  $d_{g2}$  manifold.

The existence of charge-density waves (CDW) has been demonstrated in  $2H\text{-TaSe}_2$ .<sup>1,2</sup> A transition from a high-temperature Kohn metal to an incommensurate CDW has been found at  $T_0 = 122.3^\circ\text{K}$ . A second transition, to a commensurate  $3 \times 3$  superlattice, occurs at  $T_d = 90^\circ\text{K}$ . Conductivity and susceptibility data<sup>1</sup> indicate that the amount of destruction of Fermi surface and the overall distortion magnitude are very small upon CDW formation. This behavior is similar to that of  $2H\text{-NbSe}_2$  and is in contrast with CDW's in the  $1T$  polytypes, where distortion is now believed to be much larger.<sup>1,3</sup> At the CDW onset the electron

band structure undergoes changes that are related to the formation of a smaller Brillouin zone. A folding back of bands takes place, accompanied by the appearance of new gaps, particularly in the neighborhood of the Fermi surface. A change is therefore expected in the optical properties, which should be particularly noticeable across the transition temperatures. Preliminary indications of such changes in  $2H\text{-TaSe}_2$  have been extracted by Barker, Ditzenberger, and Di Salvo<sup>4</sup> from absolute reflectivity measurements over a broad frequency range, and in  $1T\text{-TaS}_2$  and  $1T\text{-TaSe}_2$  by Tsang and Shafer<sup>5</sup> in thermoreflectance.