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Nuclear and Electron Paramagnetic Resonance Studies of Antiferroelectric Ammonium Dihydrogen Phosphate*

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The continuous-wave deuteron magnetic resonance of $ND_4D_2PO_4$ (ADP) was investigated above and below the antiferroelectric phase transition temperature (228°K). Principal coordinate systems of the deuteron-electric field gradient tensor were determined. A large line splitting occurs below T_c owing to the localization of deuterons on phosphate tetrahedra. Smaller line splittings also occur which are due to distortions of the OD bond directions. Proton relaxation times of $NH_4H_2PO_4$ exhibit a minimum at 170°K and a discontinuity near the transition temperature ($T_c=148$°K). The discontinuity is accompanied by a change in activation energy for the NH_4^+ ion reorientation from 3.7 kcal mole^{-1} ($T>T_c$) to 4.3 kcal mole^{-1} ($T<T_c$). ADP was doped with arsenic and the electron paramagnetic resonance of the γ-irradiated material was investigated from 77 to 330°K. A transition of the triplet-proton hyperfine structure to a quintet was observed in the vicinity of 300°K. The measurements performed show that the proton orientations and dynamics are very similar to those observed for potassium dihydrogen phosphate (KDP) and that the main difference in dielectric behavior between ADP and KDP results from the reversal of Slater energies of proton configurations about the phosphate tetrahedra. The energy reversal appears to be due entirely to the ammonium ions.

I. INTRODUCTION

AMMONIUM dihydrogen phosphate (ADP) undergoes an antiferroelectric phase transition[1,2] at 148°K with a concomitant change in crystal symmetry from tetragonal $I\bar{4}2d$ to orthorhombic $P2_12_12_1$.[3] ADP at room temperature is isomorphous to potassium dihydrogen phosphate (KDP); however, the phase transition is antiferroelectric rather than ferroelectric and the dominant anomaly in the dielectric constant occurs along the crystal a axis rather than the c axis as in KDP.[1] KDP has been studied by deuteron[4] and proton[5] magnetic resonance. The results of these experiments clearly show that above the transition temperature T_c the acid hydrogens are rapidly moving between adjacent PO_4 tetrahedra and below T_c the protons are localized. Chiba[6] reported the deuteron resonance of the ammonium ion in ADP both above and below T_c which indicated a distortion of the ammonium ion occurs at the transition. Blinc and co-workers[7] studied the temperature dependence of the electron paramagnetic resonance (EPR) of neutron-irradiated potassium dihydrogen arsenate (KDA). KDA is similar to KDP in dielectric behavior. At low temperatures, a triplet-proton hfs was observed from the AsO_4^{4-} radical produced by the irradiation. At temperature well above T_c, a quintet structure was observed. This result indicates the absence of a "ferroelectric mode" instability for the hydrogen atoms which would result in an abrupt change of the hyperfine pattern at the transition temperature.[7] In the present experiments, all of these resonance techniques have been applied to ADP in an endeavor to detect a behavior of protonic orientation and motion which would distinguish ADP- from KDP-type ferroelectrics.

II. EXPERIMENTAL PROCEDURE

Deuterated ADP was obtained by successive (threefold) isotope exchange of ordinary ADP with D_2O. Single crystals were then grown by slowly cooling seeded solutions of $ND_4D_2PO_4$ in D_2O. Crystals axes were identified from the known habit of the crystal and from Laue photographs with forward scattering.

Dielectric constant measurements were used to determine the Curie temperatures of the ADP single crystals studied. The dielectric constants were measured at 1000 cps, using a General Radio 716-C capacitance bridge. The crystals were painted with DuPont No. 4922 silver paint to form the capacitor plates. Since the percent deuteration for the crystals varied somewhat, producing a consequent range of Curie temperatures, all of the low-temperature deuteron resonance measurements were made at $T=-65$°C to insure that they were performed in the antiferroelectric phase.

Proton spin-lattice relaxation times T_1 were measured by a 180°–90° pulse sequence at 42 MHz, using an NMR Specialties model PS-60A pulsed spectrometer, Varian Associates 12-in. electromagnet, and variable temperature apparatus. Relaxation times along the

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TABLE I. Principal components (in kHz) of quadrupole-coupling tensors ($V_{ii}=eQ\phi_{ii}/\hbar$) and their orientations.

Temp (°C)	Type	$\lvert V_{zz}\rvert$ (θ_z, φ_z)	$\lvert V_{yy}\rvert$ (θ_y, φ_y)	$\lvert V_{xx}\rvert$ (θ_x, φ_x)
25	x	118 (90°, −2°)	62 (2°, −96°)	56 (92°, −92°)
	y	120 (90°, −93°)	61 (6°, −179°)	59 (84°, −3°)
−65		131 (90°, 0°)	72 (25°, 90°)	59 (65°, −90°)
25[a]		120 (90°, 0°)	63 (0°, −)	57 (90°, 90°)

[a] Reference 6.

rf field ($T_{1\rho}$) were measured by a 90° pulse followed by a pulse shifted 90° in phase and of variable time duration.

Deuteron magnetic resonance was observed near 6 MHz, using a conventional Varian Associates V4200B nuclear induction spectrometer. In order to observe the resonance of the acid deuterons, a relatively high (~1 G) rf field was used and the dispersion mode signal was observed. A Varian Associates C-1024 Time Averaging Computer was employed to improve the signal-to-noise ratio in the conventional manner. A Harvey-Wells NMR proton gaussmeter was used to calibrate and monitor the magnetic field. The crystals were rotated about the twofold axes *a*, *b*, *c*, and the quadrupole coupling tensor was determined by the Volkoff method.

ADP and KDP (KH_2PO_4) crystals were grown from aqueous solutions in the presence of ~10% AsO_4^{3-}. These crystals and ADA showed intense electron-resonance signals at room temperature after γ irradiation. The electron resonance was observed near 9 kMHz with 100 kHz modulation. Since we are only interested in the motions of protons, it was necessary to use only one orientation $H \parallel c$.

III. RESULTS

A. Deuteron Magnetic Resonance

Before discussing the deuteron resonance results, we wish to point out evidence that in ADP the largest component (ϕ_{zz}) of the electric-field gradient (EFG) tensor ϕ will be in the direction of the OD-bond axis within about 1°. In the gaseous D_2O molecule microwave rotational spectroscopy[8] indicates that the deviation between the *z* principal axis of the EFG tensor and the O-D direction is 1°. Bjorkstam's[4] results on the *z* principal axis directions of the OD bonds in KDP agree with the neutron-diffraction OH directions[9]

TABLE II. Splittings of rotation patterns about crystallographic axes, −65°C.

Axis of rotation	x	y
a	···	±3°
b	±5°	···
c	±3°	±4°

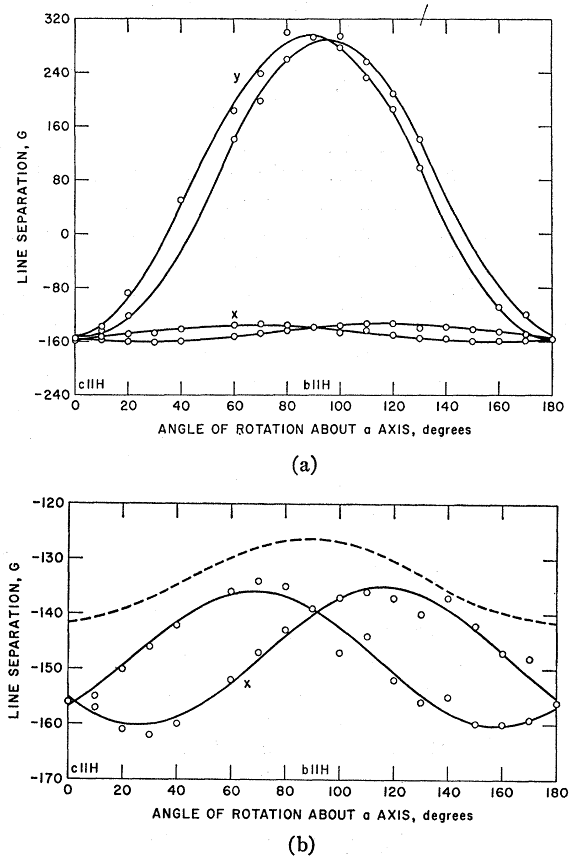

FIG. 1. (a) Deuteron-resonance line separation at −65°C versus angle of rotation about the crystal *a* axis. Solid curves are least-squares fits of the data. There are two *x* lines and two *y* lines due to localization of deuterons on phosphate tetrahedra; (b) lower portion of (a) on an expanded scale. Dashed curve is the least-squares fit of the corresponding data at 25°C.

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within experimental error (±1°). This conclusion is of importance in the present work since significant deviations of the z principal axes from the principal crystallographic directions are observed in ADP.

Results for the principal components and directions of principal axes are given in Table I at 25° and −65°C. The values given for −65°C are averaged with respect to small splittings which occur in rotation about each of the principal crystallographic axes. Principal axes of the remaining three OD bonds are obtained by reflection in the ab plane and also by rotation about the c axis by 90°. The observed small splittings of the resonance lines in rotation about various axes are given in Table II. Here "splitting" refers to a single-deuterium line which splits up into two lines with a small separation below T_c. In Tables I and II the polar directions and axes and designation refer to the original a and b axes at room temperature. On cooling a crystal through the transition shattering occurs and a 90° twinned crystal is obtained with random 90° reorientations of the original a and b directions. x refers to the OD bonds along the original a axis of the crystal and y to those along the b axis. In Fig. 1(a) is shown the rotation pattern about the crystal a axis and in Fig. 1(b) the lower portion of Fig. 1(a) is shown on an expanded scale.

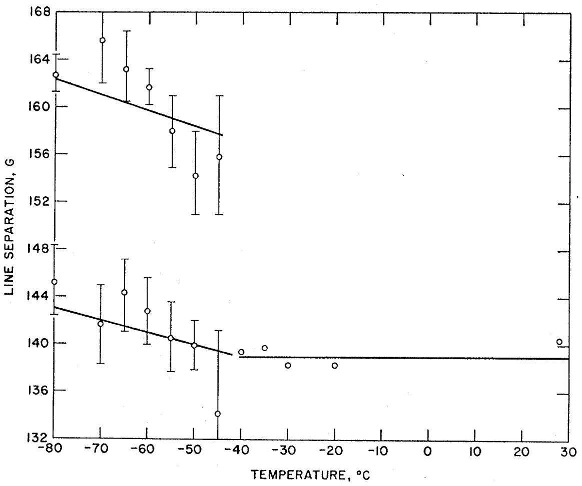

FIG. 2. Temperature dependence of the x-bond line separation in rotation about the a axis versus temperature with the magnetic field directed 40° from the c axis.

The high-temperature (25°C) spectra result from an averaging of the low-temperature pairs related by reflection in the ab plane of the crystal if a 10% increase in coupling constant V_{zz} is taken into account. This is clearly seen in Fig. 1(b), where the dashed curve is the high-temperature rotation pattern and is the average of the two low-temperature patterns. A similar effect was found in KDP by Bjorkstam,[4] where the increase in V_{zz} was somewhat less (7%). To a first approximation one expects the direction of V_{yy} to correspond to the normal to the plane formed by an oxygen atom and the nearest-neighbor phosphorous and deuteron atoms. In ADP these directions are at angles of ±(25±3)° with respect to the c axis and from x-ray diffraction data[3] we calculate these angles as ±33°. A deviation of 5° of the direction of V_{yy} from the P-O-D plane was

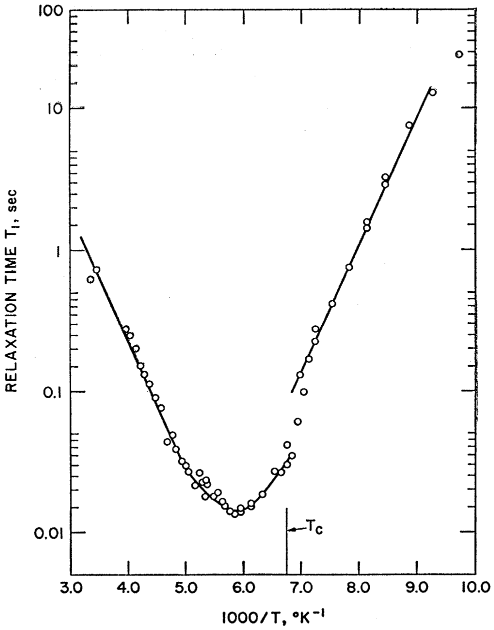

FIG. 3. Proton spin-lattice relaxation time versus reciprocal temperature at 42 MHz.

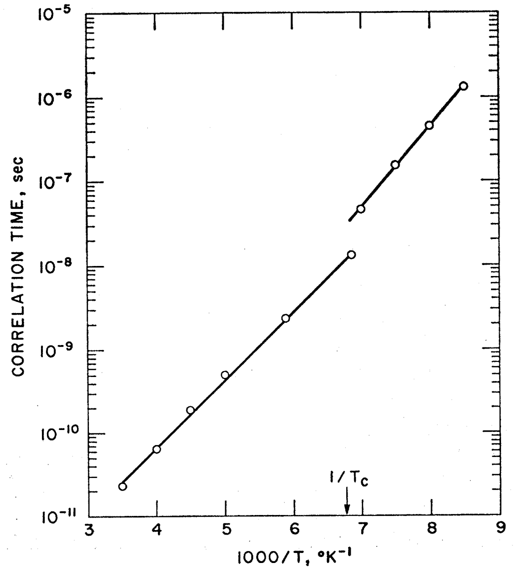

FIG. 4. Correlation time for ammonium-ion reorientation versus reciprocal temperature.

TABLE III. Activation energies and pre-exponential factors for NH_4^+ ion.

	$T<T_c=148$°K	$T>T_c=148$°K
ΔE, kcal	4.3 ± 0.3	3.7 ± 0.3
τ_c^0, sec	3×10^{-14}	5×10^{-14}

found in KDP.[4] The small splittings listed in Table II are not present in the high-temperature phase. These splittings we believe are due to a deviation of the O-D bond directions from the crystallographic axes. The bonds are tilted up or down with respect to the *ab* plane (±4° average) and laterally with respect to the *a* axis (±3°) or *b* axis (±4°). These latter splittings appear to result from the 90° twinning of the crystal and would occur if, in an individual crystallite, the O-D bonds are not aligned precisely along the crystal axes. No such deviations were found in KDP.

As in KDP, the splitting of the x-bond resonance lines observed in rotation about the crystal *a* axis (or *y* bond lines observed in rotation about *b*) is due to a localization of deuterons on phosphate tetrahedra. Above T_c, a deuteron rapidly moves from one end to the other of the ODO array at a rate rapid compared to the *difference* in resonance frequency of D when attached to either oxygen. From Fig. 1(b), the maximum value of the difference may be seen to be approximately 15 G or 10^4 rad sec^{-1}. The temperature dependence of the x-bond splitting in rotation about the *a* axis is shown in Fig. 2.

No evidence for a coexistence of the high- and low-temperature phases was found within $\pm\frac{1}{2}$°C of the phase transition. This is in contrast to the KDP results, where a temperature interval of $\frac{1}{2}$°C both the high- and low-temperature lines were found to coexist.[4]

The lower limit given above for the rate of deuteron transfer ω_t between neighboring phosphate tetrahedra is consistent with the results of Section III C, where it is shown that $\omega_t=2\times10^8$ sec^{-1} at 294°K in ordinary ADP.

B. Proton-Relaxation Times

Measured spin-lattice relaxation times T_1 are given in Fig. 3. As indicated in the figure, the T_1 data show a discontinuity in the vicinity of the reported[1] phase-transition temperature. Correlation times were calculated from the T_1 data from an expression previously reported[10] for the NH_4^+ relaxation time and are plotted in Fig. 4. Activation energies and pre-exponential factors derived from the correlation times are given in Table III. The transition is accompanied by an abrupt increase in activation energy for the ammonium-ion reorientation from 3.7 to 4.3 kcal mole^{-1}. Measured relaxation times along the rf field were consistent with the T_1 data.

C. Electron-Paramagnetic Resonance

Line shapes were computed from the formalism given by Blinc *et al.*[7] for the EPR of the AsO_4^{4-} center coupled by hyperfine interaction to the acid protons. In Table IV are listed the temperatures T_t for which the correlation time for protonic motion is equal to ω_t the reciprocal of the hyperfine coupling constant (2×10^8 sec^{-1}) for KDP, ADP, ADA, and KDA. This temperature will be considered as the transition temperature for the quintet line shape to convert to the triplet line shape and is determined by comparison of the computed line shapes with the observed line shapes. Also listed is the Curie temperature T_c and the ratio T_t/T_c. Although the ratio T_t/T_c shows considerable variation for the salts listed in Table IV, there is no apparent correlation with the ferro- or antiferroelectric nature of the phase transitions. The data do indicate that the proton dynamics above T_c are very similar in KDP and ADP.

IV. DISCUSSION

As is evident from Fig. 4, the ammonium ion undergoes an abrupt change in rate of reorientation at the transition temperature. The pre-exponential factors given in Table III are well within order-of-magnitude agreement with those calculated from a classical rotator model.[10] The change in activation energy appears to be associated with the anomalous transitional entropy ΔS in ADP. Nagamiya[2] calculated 0.80 cal °K^{-1} mole^{-1} for ΔS due to the disordering of the acid hydrogens; the experimental value[11] is 1.05 cal °K^{-1} mole^{-1}. The excess entropy was associated by Nagamiya with "configurational changes in the ammonium ions." At least a part, if not all, of the entropy change may be explained as due to the increase of entropy associated with the decrease of the frequency of torsional oscillations of the ammonium ions associated with the lowered barrier height. As a first approximation, let us assume that the change in torsional oscillation fre-

TABLE IV. Triplet-to-quintet transition temperatures.

Salt	T_t	T_c	T_t/T_c
KH_2PO_4-As	206	123	1.68
$NH_4H_2PO_4$-As	294	148	1.98
$NH_4H_2AsO_4$	318	216	1.47
KH_2AsO_4	225	97	2.32

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quency is directly proportional to the change in activation energy. Let us represent the NH_4^+ torsional oscillator as a harmonic oscillator for which the entropy is[12]

$$S=R\{x/(e^x-1)-\ln(1-e^{-x})\}, \qquad (1)$$

where $x=h\nu/kT$ and ν is the frequency separation between levels. For NH_4^+ ion reorientations $x\approx 1$ at T_c and hence $\Delta S\approx 0.2$ cal °K^{-1} mole^{-1}, in close agreement with the observed anomalous entropy of ADP.

The relatively large splittings in the deuteron resonance of the antiferroelectric phase of ADP probably is associated with the greater crystal distortions in ADP as compared to KDP. As pointed out by Nagamiya,[2] the transition in ADP may be explained by a reversal in the ordering in energy of the Slater configurations of protons on a PO_4 tetrahedron. This effect appears to be due almost exclusively to the ammonium ions since substitution of Tl^+ for NH_4^+ in ADP alters the transition temperature and above 33% of Tl results in normal dielectric behavior.[13] As indicated clearly by the electron-resonance results, the proton dynamics do not change greatly from KDP and the entire difference between the dielectric behavior of KDP and ADP may be ascribed to the reversal of Slater energies of proton configurations about the phosphate tetrahedra.

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Metamagnetism in Eu_3O_4

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The magnetic properties of the metamagnet Eu_3O_4 are analyzed using molecular-field theory. For the antiferromagnetic ground state, it is assumed that linear, ferromagnetic chains of spins (Eu^{2+}) are polarized along the c axis of the orthorhombic unit cell, with neighboring chains antiparallel. The weakly magnetic ions Eu^{3+} provide an apparently inert magnetic background. Exchange constants are deduced from the paramagnetic Curie temperature $\theta_p=5$°K and the critical field $H_c=2.4$ kOe. The constants for first- and second-neighbor Eu^{2+} interactions are $J_1/k\sim 0.3$°K and $J_2/k\sim -0.02$°K, respectively. An anisotropy field of 7 kOe is derived from the transverse magnetic susceptibility at low temperatures. This value is also obtained from a magnetic dipolar sum. Theoretical estimates of the ordering temperature give $T_c\sim 5$°K, as observed.

I. INTRODUCTION

METAMAGNETIC behavior has been observed in Eu_3O_4 at liquid-helium temperatures.[1] The magnetic ordering has been interpreted,[1] tentatively, with a simple, "linear-chains" model for the magnetic structure. In this paper, the model will be treated in more detail. It will be shown to provide a satisfactory description of the experimental parameters, T_N, θ_p, H_c, and H_A (Néel point, paramagnetic Curie point, critical field, and anisotropy field, respectively). The influence of trivalent europium on the magnetic properties of this oxide will be carefully considered.

This study of metamagnetism in Eu_3O_4 provides new information on interactions in magnetic compounds of the form AB_2O_4. It will be shown that the exchange interactions are predominantly ferromagnetic in Eu_3O_4, despite the antiferromagnetic ground state. Useful comparisons are made with the properties of the isomorphous oxides,[2] $SrGd_2O_4$ and $SrEu_2O_4$, and chalcogenides,[3] EuL_2X_4, with $L=$ Lu, Y, Sc and $X=$ S, Se.

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