D and ^{14}N Quadrupole Interaction in the Ammonium Ion of Ammonium Dihydrogen Phosphate

By Takehiko CHIBA

(Received August 25, 1964)

The deutron magnetic resonance (DMR) of ND_4 in a single crystal of $ND_4D_2PO_4$ (ADP) was measured in the paraelectric phase at room temperature and in the antiferroelectric phase at about $-40°C$. The ^{14}N resonance of ADP was also measured at room temperature. The observed quadrupole couplings are given in Table I. Lowering the temperature through the phase-transition temperature shatters a single crystal, but the fragments are held together, keeping the original crystal shape. It is known[1] that each fragment is oriented with its a or b axis parallel to the axis direction of the original high-temperature form. The spectra, therefore, correspond to a superposition of those two crystals which are oriented perpendicular to each other. It was then possible to determine eqQ and the orientation of the field gradient (f. g.) tensor of the low temperature phase, except that there remains a choice of two alternatives of the a and b axes to which the f. g. tensor is referred, from the observed spectra with the help of symmetry considerations and the powder spectrum.[2]

TABLE I. QUADRUPOLE COUPLING, ASYMMETRY PARAMETER AND THE DIRECTION COSINES OF FIELD GRADIENT TENSOR OBSERVED IN AMMONIUM DIHYDROGEN PHOSPHATE

Ammonium D

Room temp. $eqQ/h=3.4$ kc., $\eta=0$.
F. g. parallel to c axis.

$-40°C$ $eqQ/h=6.0$ kc., $\eta=0.89$.

F. g. component*	a (or b)	b (or a)	c
1	0.226	0.413	0.882
2	0.681	0.580	-0.447
3	-0.696	0.702	-0.150

And three other sets of f. g. direction cosines which differ from the one listed by the sign of either a, or b, or c axis components.

^{14}N

Room temp. $eqQ/h=24.6$ kc. ($NH_4H_2PO_4$) $\eta=0$.
F. g. parallel to c axis.
$eqQ/h=27.3$ kc. ($ND_4D_2PO_4$)

* F. g. components 1, 2 and 3 are in the order of the largest absolute value.

In general, except at very low temperatures, a large part of the quadrupole coupling of the D of an ND_4^+ ion is cancelled because of the rapid interchanges of its four deuterons, leaving the small fraction due to the deviation from the exact tetrahedral symmetry of the ion. On some ammonium salts DMR was measured and the results compared with the calculated f. g. from the point charge approximation, assuming a net charge located at the center of ND_4^+. The results were not in agreement with the observed value, although the magnitude of the calculated f. g. was of the right order. In the paraelectric phase of

---

1) E. A. Wood, W. J. Merz and B. T. Matthias, *Phys. Rev.*, **87**, 544 (1952).

2) T. Chiba, *J. Chem. Phys.*, **36**, 1122 (1962).

ADP the hydrogen positions have been determined by neutron-diffraction study.[3] The point charge calculation was carried out, taking hydrogen positions into account, to see if any better result can be obtained. In the present case the f. g. at a deuteron of ND_4^+ is axially symmetric about the c axis, so that only the f. g. component in that direction need be considered. The calculation was made* by taking all atoms within a sphere of 46 Å (6-unit-cell distance) into account, by assuming charges for NH_4, H (acid), and PO_4 of $+e$, $+e$ and $-3e$ respectively, and by assuming parameter α to be the fraction of $+e$ on N and β, that of $-3e$ on P ($1\geq\alpha$, $\beta\geq0$). For those atoms outside 25 Å (3-unit-cell distance), α and β are set equal to zero. The same calculation was made at a nitrogen position. For the f. g. at a hydrogen position the effect of the directly-bonded nitrogen atom was excluded. Similarly for the f. g. at a nitrogen atom, the effect of directly-bonded hydrogens was excluded. The results are given by V_h and $V_{h'}$ at hydrogen and by V_n at nitrogen in the following equations (in units of $e/\text{Å}^3$).

$$V_h = -0.0079 - 0.0022\alpha - 0.0903\beta \qquad (1)$$

$$V_{h'} = -0.0152 + 0.0051\alpha - 0.0403\beta \qquad (2)$$

$$V_n = -0.0534 - 0.0033\alpha - 0.0612\beta \qquad (3)$$

V_h gives the value without the contribution to f. g. from the three hydrogen atoms which are bonded to the same nitrogen atom, and $V_{h'}$, that including it. The fact that the difference between the values of the calculated f. g. for a hydrogen and for a nitrogen (V_h and V_n) is rather large indicates the strong dependence of this quantity on the atomic coordinates. The order of magnitude of the calculated f. g. is about the same as that in the previous paper. The observed eqQ of 3.4 kc. corresponds to a field gradient of (±) 0.035 if the polarization effect[2] is disregarded. This can be fitted by Eq. 1 or 2 with reasonable values of parameters α and β. The difficulty arises when one compares Eq. 3 with the observed values. For nitrogen, the antishielding factor is not well known. However, Kanda gave an estimate of about 47 in the state of the NH_4^+ ion.[4] If one assumes this value, the observed f. g. will be (±)0.0006.** Equation 3 gives far too large an f. g. with any set of α and β for the experimental value to be accounted for. Point charges at the four directly-bonded hydrogen atoms make an f. g. contribution of $-0.031(1-\alpha)$ at nitrogen, which only increases the discrepancy. This means an inadequacy of the point charge approximation in the present case. The reason why it fails most likely lies in the evaluation of the contribution from the neighboring atoms. However, there might be another reason, namely, that the charge distribution is diffuse in nature, as has been noted in the crystal analysis of ammonium bifluoride,[5] so that the f. g. arising from the crystalline field is actually much smaller. Therefore, it may be more reasonable to relate the observed eqQ of deuteron, simply neglecting the effect of the long-range crystalline field, as in the previous paper, to the f. g. in each N–D bond direction which deviates from that of a regular tetrahedron by 2.0° as determined by neutron diffraction. That is, $3.4\text{ kc.} = (eq_0Q_D/h)\times 2\sqrt{2/3}\times 2.0\pi/180$, which leads to $eq_0Q_D/h = 130$ kc. Considering the facts that an N–D···O hydrogen bond is present[3] and that a hydrogen bond tends to decrease eqQ, this value appears reasonable. For the f. g. at nitrogen, the observed value is so small that one needs to take the f. g. contribution from the crystalline field into consideration. Then one has to assume that there is a rather accidental cancellation of this effect by that due to the electronic configuration of the NH_4^+ ion. This point may be cleared up if the eqQ_N values of other ammonium salts are measured.

Although the displacements of atoms in the ADP crystal due to the transition from the para- to the antiferroelectric phase have been determined for heavier atoms,[6] those for the hydrogen atoms are not known. Therefore, the calculation of f. g. values for the antiferroelectric phase could not be made. However, the large quadrupole coupling seems to indicate a greater distortion of the ND_4^+ ion in this phase than in the paraelectric one.

The Institute for Solid State Physics
The University of Tokyo
Azabu, Tokyo

---

[3] L. Tenzer, B. C. Frazer and R. Pepinsky, *Acta Cryst.*, **11**, 505 (1958).

* The PC-2 electronic computer was used for the calculation.

[4] T. Kanda, presented at the 1962 Fall Meeting of the Physical Society of Japan.

** A Q_{14} value of 0.02×10^{-24} cm^2 is assumed.

[5] T. R. R. McDonald, *Acta Cryst.*, **13**, 113 (1960).

[6] R. O. Keeling, R. Pepinsky, *Z. Krist.*, **106**, 236 (1955).