FIG. 1. Chamber for measurement of recoil-ion current.

After completion of the current measurements, tank argon was admixed with active gas, and a small aliquot, approximately  $10^{-4}$ , was transferred into a calibrated proportional counter for determination of the absolute disintegration rate. Corrections were made to the measured counting rate value for L capture<sup>3</sup> and for the limited absorption of the chlorine fluorescence radiation, the yield of which was taken to be 0.083.4

The ratio of the current to the disintegration rate is the average charge per disintegration. In the decay of A<sup>37</sup> it is found that the average charge on the Cl<sup>37</sup> product ion is  $+3.85\pm0.2$ .

Experiments with other radioactive substances are being carried out, and a more detailed account of the work will be published.<sup>5</sup>

The authors are indebted to R. W. Dodson and A. O. Allen of this laboratory who suggested the experimental method used in discussions during the summer of 1951.

† Research carried out under the auspices of the AEC.
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<sup>8</sup> S. Wexler of the Argonne National Laboratory has recently informed us that he is engaged in work of a very similar nature.

## Polymorphism of ND<sub>4</sub>D<sub>2</sub>PO<sub>4</sub>

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T is well known that  $NH_4H_2PO_4$  and  $ND_4D_2PO_4$  play a special role in the inner role in the isomorphous series of XH<sub>2</sub>PO<sub>4</sub> and XD<sub>2</sub>PO<sub>4</sub> crystals<sup>1</sup> (X=NH<sub>4</sub>, K, Rb). All members of the series go through a polymorphic transformation at low temperatures. Below this the K and Rb salts become ferroelectric, but the  $\mathrm{NH}_4$  salts do not.

Matthias showed<sup>2</sup> that the substitution of hydrogen by deuterium in the ammonium salt raises the transition temperature by about 90°. The same shift has been observed for the Curie point of the ferroelectric potassium and rubidium salts. This fact and the observation that the specific heat anomaly at the transition of the NH4 salt is about the same as the ones of the K and

Rb salts at their Curie points3 indicates that in the ammonium salts we also have to deal with a hydrogen bond rearrangement.

By using Slater's picture<sup>4</sup> it can be shown that there are 3 possibilities of dipole alignments: first, a parallel alignment in the c direction (ferroelectric case as in K and Rb salts); second, an antiparallel arrangement in the a-direction; and third, an alignment involving two directions whose resultant would give a [110] effective polarization. Since no spontaneous polarization is found in these crystals below the transition it seems very likely that the ammonium salts show the second type of arrangement, namely, an antiparallel alignment of dipoles in the a direction.

The tetragonal crystals of  $ND_4D_2PO_4$  have a c/a ratio of  $1.003 \pm 0.0005$  at room temperature, while that of NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> is 1.0058.5 The lattice constants of the heavy salt at room temperature are a = 7.510,  $c = 7.535 \pm 0.005$ A.

At approximately -30°C crystals of ND<sub>4</sub>D<sub>2</sub>PO<sub>4</sub> go through a polymorphic transformation which shatters large crystals, but fragments large enough for observation with the polarizing microscope remain intact and the transformation has been repeatedly observed. The low temperature form has slightly lower birefringence than the high form and a clearly defined boundary between the two moves across the crystal as the transformation takes place. There is no change in extinction direction. These observations were made on about twenty fragments, sealed in a partially evacuated tube to avoid H<sub>2</sub>O contamination.

A single fragment with major surfaces parallel to (001) and with one (100) bounding surface was sealed beneath a cover glass for observation of the optical interference figure. At the transition the negative uniaxial figure of the high form opens out into a negative biaxial figure with  $(-)2V = 18^{\circ} \pm 5^{\circ}$ . The acute bisective in the low form replaces the single optic axis in the high form, i.e., is parallel to c, and the optic plane is parallel to a {100} plane of the high form. The low form is thus orthorhombic with its crystallographic axis parallel to those of the high form, unlike the K and Rb salts where the transformation involves a shear in the (001) plane so that the orthorhombic a and b axes are at  $45^{\circ}$  to the tetragonal a axes.

The space group of the high form is  $D_{2d}^{12} - I\overline{4}2d$ . The powder photograph of the low form, however, shows additional weak lines for which  $(h^2 + k^2 + l^2)$  is odd, indicating that it is no longer body-centered. The crystal is still piezoelectric. The space group of the low form is therefore probably  $D_{2^4}-P2_12_12_1$ . This means that the PO<sub>4</sub> group at  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$  is no longer equivalent to the PO<sub>4</sub> group at 000, as it would be (1) if the deuterium ions were centrally located between their neighboring oxygens as they are in the high form, or (2) if the crystal were ferroelectric along the c axis. The dipole arrangement giving a [110] resultant polarization is also incompatible with this symmetry.

Thus the electrical measurements and the x-ray diffraction and optical data independently indicate the presence of an antiferroelectric a (or b) axis in the low temperature form of ND<sub>4</sub>D<sub>2</sub>PO<sub>4</sub>.

It is of interest in this connection that in the K and Rb salts the thermal expansion coefficient for the c axis is greater than that for the a axis, whereas in the NH<sub>4</sub> salts the reverse is true.<sup>6</sup>

At  $-53^{\circ}C \pm 8^{\circ}$  the lattice constants of ND<sub>4</sub>D<sub>2</sub>PO<sub>4</sub> are a = 7.48 $\pm 0.02$ ,  $b = 7.48 \pm 0.02$ ,  $c = 7.53 \pm 0.02$ . The orthorhombic departure from tetragonal symmetry, which we know from the optical observations must exist, was not observable. Lattice parameter differences of 0.02A could have been detected. No marked intensity differences were observed between the ND4D2PO4 powder picture taken at room temperature and that at -53 °C.

The indices of refraction of ND<sub>4</sub>D<sub>2</sub>PO<sub>4</sub> at 20°C are N = 1.479 $\pm 0.003$ ; N = 1.518 $\pm 0.003$ .

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