

value of the spin of Ti of either 3.1 ± 0.4 or 3.7 ± 0.4 , depending upon whether the isotopic abundance is taken to be that of Ti^{47} or Ti^{49} , respectively. This would indicate that the spin is probably $7/2$ and that the signals are probably due to Ti^{49} instead of Ti^{47} , although this measurement is not conclusive because of uncertainties in the degree of dissociation. From the observed optimum signal to noise ratios of the Ti resonances in various samples we can also estimate the spin to be $7/2 \pm 1$. Since we have observed the magnetic moment to be negative, this indicates an $f_{7/2}$ state for the odd neutron, which is not in disagreement with the predictions of the nuclear shell model.⁶ Assuming, then, that the spin is $7/2$ we find from (1) that the diamagnetically uncorrected value of the magnetic moment of Ti^{49} (or perhaps Ti^{47}) is

$$\mu_{Ti} = -(1.1022 \pm 0.0003) \text{ nm}, \quad (2)$$

where we have taken the proton moment to be 2.7925 nm. We have searched over a wide region for the resonance signal from the other odd Ti isotope, but have as yet failed to find it, probably because the gyromagnetic ratio is small.

We have observed the nuclear magnetic resonance of As^{75} in a 1.2 molar aqueous solution of Na_3AsS_4 and also in a basic aqueous solution of Na_3AsO_4 . The Na_3AsS_4 sample gives a large signal, with a half-width of about 0.7 gauss; the line width is limited by quadrupole broadening, which is not excessive in this case because the sample is well dissociated into symmetric $(AsS_4)^{--}$ ions. On the other hand, it was found that in the Na_3AsO_4 sample the As resonance signals were obliterated by excessive quadrupole broadening unless the sample was made basic (by the addition of NaOH) to a $pH \approx 12$. This is in agreement with the chemical evidence that Na_3AsO_4 does not dissociate into $(AsO_4)^{--}$ ions, except in basic solution.⁷ We have not detected a "chemical shift"^{7b} between the As resonance frequencies in $(AsS_4)^{--}$ and $(AsO_4)^{--}$. The ratio of the As^{75} resonance frequency to that of protons in H_2O in the same magnetic field has been found to be

$$\nu_{As^{75}}/\nu_H = 0.17129 \pm 0.00003. \quad (3)$$

The spin⁸ of As^{75} is known to be $3/2$, and we have verified this by comparing the As^{75} signal from Na_3AsS_4 to the D^2 signal in D_2O ; our experimental result is $I(As^{75}) = 1.5 \pm 0.2$. Taking the proton moment to be 2.7925 nm, we find from (3) the diamagnetically uncorrected value of the moment of As^{75} to be

$$\mu(As^{75}) = +(1.4350 \pm 0.0003) \text{ nm}. \quad (4)$$

This value is in agreement with that recently reported by Dharmatti and Weaver.⁹

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The Nuclear Magnetic Moment of Tc^{99} *

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THE nuclear resonance of long-lived radioactive Tc^{99} has been observed in a nuclear induction apparatus of the type originated by Bloch and similar to that recently described by Proctor.¹ The sample contained 156 mg of Tc^{99} , as NH_4TcO_4 , in an aqueous solution. The Tc^{99} was isolated from fission products by one of us (W.J.M.). One ml of D_2O was added to the solution

giving a total volume of 6 ml, and all frequency ratio measurements were relative to deuterium. Frequency measurements were made with a Signal Corps type BC-221 frequency meter calibrated with harmonics from an external 100 kc, crystal-controlled oscillator which in turn was compared with the National Bureau of Standards radio station WWV at 5 Mc. Frequencies were measured at nominal fields of 7200 and 8300 gauss giving

$$\nu(Tc^{99})/\nu(D) = 1.46628 \pm 0.0001.$$

With Levinthal's² deuteron-to-proton frequency ratio of 0.1535059, the above ratio yields the following frequency ratio relative to the proton,

$$\nu(Tc^{99})/\nu(H) = 0.22508.$$

With a Tc^{99} diamagnetic correction of 0.411 percent,³ a spin of $9/2$ for Tc^{99} ,⁴ and a value of 2.79268 nuclear magnetons⁵ for the proton moment, this ratio gives the following value of the nuclear magnetic moment, in units of the nuclear magneton

$$\mu(Tc^{99}) = +5.6805 \pm 0.0004.$$

The indicated estimated accuracy of the above value does not include the uncertainty in the diamagnetic correction. The sign of the Tc^{99} magnetic moment was obtained by comparison with D, which is known to be positive.¹

A previous measurement of the nuclear magnetic moment of Tc^{99} by Kessler and Meggers⁶ made by optical spectroscopy gave 5.2 ± 0.5 nuclear magnetons, which may be increased 10 to 20 percent by additional corrections. This value is consistent with the more accurate value reported above.

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Structural Changes in the Ferroelectric Transition of KH_2PO_4 *

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AS the temperature is lowered through the ferroelectric Curie point ($122^\circ K$), KH_2PO_4 changes from the tetragonal $I42d$ (or $F4d2$) symmetry to that of the orthorhombic space group Fdd . This was established in the earlier x-ray investigation of de Quervain¹ and of Ubbelohde and Woodward.² These authors also accurately measured the lattice deformation and noted that changes in intensity were observable in some of the diffraction maxima. De Quervain measured a few of the intensities from room temperature down past the transition. Working on the basis of the well-known room temperature determination of the tetragonal structure by West,³ he suggested a model for the ferroelectric structure involving displaced P's in deformed PO_4 groups; however, he had an insufficient number of observations (and these were not from the most favorable class of reflections) to test his model.

We undertook a more complete attack on this problem with the purpose of determining the atomic rearrangements associated with the transition. Of specific interest was the detection of relative displacements of the constituent ions parallel to the polar c -axial direction. It should be mentioned here that the Slater⁴ theory of the transition, while very probably playing an important role, cannot in itself account for the polarization of the crystal. It is reasonable to suppose that his scheme of hydrogen bond orientation does occur, but this must either "trigger" other structural changes or must itself be the result of the other changes. Of course, all of the contributing factors are not amenable to x-ray analysis,

but measurements of any changes in atomic positions are obviously of prime importance to the formulation of a more complete theory of ferroelectricity in the KH_2PO_4 class of ferroelectrics. Such changes have been found in our study, and these are presented briefly in this letter. Only minor refinements of secondary importance to the physical picture of the transition remain to be considered. Publication of a complete paper is being deferred until these have been checked.

The procedure followed was that of solving the tetragonal structure just above the Curie temperature, and then using these results to proceed to the more difficult structure just below. The observation temperatures were 126°K and 116°K. Intensities from a small single crystal were recorded photographically, and for any one oscillation range the observations at the two temperatures were recorded side-by-side by use of a movable camera in conjunction with a multi-layerline shield. The problem of spot splitting and superposition of nonequivalent reflections caused by domain structure was eliminated by choosing the base diagonal of the "F" cell as rotation axis. This will be discussed in more detail in the full publication. The tetragonal structure was re-determined at 126°K (instead of working from West's structure) for several reasons: (1) to study temperature corrections for the intensities, (2) to discover any changes relative to the room temperature structure that might be important to the transition, (3) to provide a closer comparison to the 116°K structure. One of the significant results was that of finding that a rather strong anisotropy in thermal vibrations had developed along the c -axis, in which direction the crystal spontaneously polarizes at the transition temperature. This was corrected for in the calculated structure factors rather than the observed.

The results of the two structure analyses and West's room temperature structure are compared in Table I. The interatomic distances are based on the tabulated cell dimensions. Those for the room temperature structure are not the ones presented in West's paper, but are obtained from the more accurate values found by Ubbelohde and Woodward by transforming from the "I" to the "F" cell. A combination of the thermal contraction data of these authors with that of de Quervain was found to check very well for the low temperature values.

The O, O distance refers to oxygens of the same elevation in the c -direction for a given PO_4 group. O, O' refers to oxygens of opposite elevation. K, O refers to distances between a potassium and closest oxygens belonging to P's having the same (x, y) coordinates as the K, while K, O' refers to closest oxygens belonging to P's displaced by $(\pm \frac{1}{2}, \pm \frac{1}{2}, \pm \frac{1}{2})$ from the K.

On cooling to 126°K it is noted that the slightly elongated O_4 tetrahedra at room temperature have become perfectly regular. A marked contraction in the hydrogen bond has occurred. It is noticeable also that while each K was surrounded by two equidistant sets of oxygens at room temperature, the K, O distances are distinctly larger than the K, O'. These elongated distances have their principal component along the c axis, which is just the direction along which the preferential thermal vibration has developed and is the direction of polarization after the transition.

TABLE I. Interatomic distances and lattice dimensions in KH_2PO_4 above and below the Curie point.

	Room temp.	126°K	116°K
Sp. Gp.	$F\bar{4}d2$	$F\bar{4}d2$	Fdd
P, O	1.56A	1.57A	(1.59A)
O, O	2.46	2.57	(1.54)
O, O'	2.60	2.57	2.55
O-H...O	2.53	2.45	2.49
K, O	2.79	2.85	(2.80)
K, O'	2.82	2.78	(2.90)
a	10.516	10.48	(2.77)
b	10.516	10.48	(2.78)
c	6.945	6.90	10.53
			10.44
			6.90

After the transition, it is seen that the O_4 tetrahedron has remained regular, but that the P's have "sagged" from their central positions. This displacement, which is parallel to the c axis, is calculated to be 0.03A. The hydrogen bond has expanded, which suggests an increased order in agreement with the Slater theory. The c -axial component of the K displacement is calculated to be 0.08A relative to the P's and 0.05A relative to the O_4 tetrahedra. This is particularly interesting not only because of the heretofore unsuspected role of the K's in contributing to the polarization, but also because their behavior suggests that they may even trigger the transition. This could be of importance in explaining the peculiarities of the $\text{NH}_4\text{H}_2\text{PO}_4$ transition.⁵ These matters will receive more attention in the complete report.

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The Production of Large Tensile Stresses by Dislocations*

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CONSIDER n similar straight parallel dislocations moving on the same glide plane; suppose that these dislocations are pushed up against an obstacle by a uniform external shearing stress t . Then Cottrell¹ and later Eshelby, Frank, and Nabarro² have shown that the force exerted towards the obstacle on the dislocation nearest the obstacle is tnb , where b is the magnitude of the Burger's vector of the dislocation. In this equilibrium situation the forward force is balanced by the force exerted by the obstacle. It is assumed in these calculations that the obstacle interacts only with the nearest dislocation. Since the forward force on a single dislocation is only tb , it is clear that such dislocation arrays are effective means for the concentration of shearing stresses. In fact, in reference 2 it is shown that the shearing stress on the glide plane ahead of the n jammed dislocations under stress t is approximately the same as that ahead of a two-dimensional crack of width $4L$ under stress t . L is the distance along the glide plane occupied by the n dislocations; L is, of course, measured along a direction perpendicular to the axes of the dislocations.

It is the aim of this letter to show that an edge type dislocation array of the type described above has large tensile stresses associated with it. It will be shown that the maximum tensile stress is of the order of nt .

Let the dislocations be numbered 0, 1, 2... j ... $(n-1)$, where the zeroth dislocation is the one nearest the obstacle. Suppose that the zeroth dislocation is at the origin of coordinates and the others are located along the plus x axis, the shearing stress t is such that it drives the dislocations towards negative x coordinates. The position of the j th dislocation is approximately given by $x_j = (\pi j)^2 A / 8nt$, where $A = Gb / 2\pi(1-\nu)$. G is the modulus of rigidity and ν is Poisson's ratio. The stresses near a single positive edge type dislocation are,³

$$\begin{aligned}\sigma_x &= -Ay(3x^2 + y^2)/r^4, \\ \sigma_y &= +Ay(x^2 - y^2)/r^4, \\ t_{xy} &= +Ax(x^2 - y^2)/r^4,\end{aligned}\quad (1)$$

where x measures the distance of the field point from the dislocation along the glide plane, y measures the distance to the dislocation normal to the glide plane, and $r^2 = x^2 + y^2$. Consider first the tensile stress σ_x in the x direction. It is clear upon examination that the largest tensile stress will be found along the negative y axis (using the coordinates described for the array).