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DETERMINATION OF THE EIGENVECTORS OF SOFT MODES  
IN  $\text{KD}_2\text{PO}_4$  AND IN  $\text{ND}_4\text{D}_2\text{PO}_4$

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**Résumé.** — Nous avons déterminé le modèle du déplacement des atomes dans le mode ferroélectrique de  $\text{KD}_2\text{PO}_4$  à l'aide de la méthode des séries de Fourier, en utilisant les diffusions inélastiques de neutrons. Pour le mode antiferroélectrique de  $\text{ND}_4\text{D}_2\text{PO}_4$  les résultats que nous avons obtenus par cette méthode n'admettent pas la présence d'un mode « d'ordre » mais il est possible que notre solution du « problème des phases » impliqué n'est pas correct.

**Abstract.** — The pattern of displacement of the atoms in the ferroelectric mode of  $\text{KD}_2\text{PO}_4$  has been determined by a Fourier series method, using neutron inelastic scattering data. For the antiferroelectric mode of  $\text{ND}_4\text{D}_2\text{PO}_4$  our results obtained by this method are inconsistent with the presence of an « ordering » mode, but our solution of the phase problem involved may not be the correct one.

The cross section for neutron scattering by a mode of vibration ( $\mathbf{q}j$ ) is proportional to  $|G(\mathbf{K}j)|^2$ , where  $G(\mathbf{K}j)$  is the structure factor for inelastic scattering. The scattering vector  $\mathbf{K}$  and phonon wave vector  $\mathbf{q}$  are related by  $\mathbf{K} + \mathbf{q} = \mathbf{H}$ , where  $\mathbf{H}$  is a vector to a point of the reciprocal lattice. (The branch index  $j$  will usually be dropped, since we shall be dealing with only one optic mode at a time). Fourier transformation gives an « eigenvector density »

$$D(\mathbf{r}) = \frac{1}{v} \sum_{\mathbf{H}} G(\mathbf{H} - \mathbf{q}) \exp(-i(\mathbf{H} - \mathbf{q}) \cdot \mathbf{r}). \quad (1)$$

The properties of this function have been discussed elsewhere [1]. In certain simplifying circumstances, which apply in the two examples given later, each atomic site  $\mathbf{r}_\kappa$  in a map of  $D(\mathbf{r})$  has a negative peak on one side and an equal positive peak on the other. The line joining the two peaks is parallel to a vector  $\mathbf{u}_\kappa$ , and (when the Debye-Waller factors of all atoms are equal) the height of each peak is proportional to  $b_\kappa u_\kappa$ , where  $b_\kappa$  is the coherent neutron scattering length for an atom of type  $\kappa$ . For a phonon mode,  $\mathbf{u}_\kappa$  is defined by

$$\mathbf{u}_\kappa(\mathbf{q}j) = m_\kappa^{-1/2} \mathbf{e}_\kappa(\mathbf{q}j) \quad (2)$$

where  $m_\kappa$  is the atomic mass and  $\mathbf{e}_\kappa(\mathbf{q}j)$  is an eigenvector of the dynamical matrix for the phonon mode involved. The  $\mathbf{u}_\kappa$  may be referred to as polarization vectors. For a phonon mode,  $G(\mathbf{K})$  involves  $\mathbf{K} \cdot \mathbf{u}_\kappa$ , while for an « ordering » mode, in which atoms move between two distinct sites,  $G(\mathbf{K})$  involves  $\sin(\mathbf{K} \cdot \mathbf{u}_\kappa)$  [2]; however over the range of  $K$  involved in our examples

these can not be reliably distinguished and the above description of  $D(\mathbf{r})$  applies as a good approximation even if the mode does not have phonon characteristics. In our examples each structure factor  $G(\mathbf{H} - \mathbf{q})$  has no imaginary component, but there is still a « phase problem » in evaluating  $D(r)$ , as in conventional crystal structure analysis, since only  $G^2(\mathbf{H} - \mathbf{q})$  is measurable.

Skalyo *et al.* [3] have measured a range of values of  $G^2(\mathbf{H})$  for the ferroelectric mode in  $\text{KD}_2\text{PO}_4$ , for which  $q \rightarrow 0$ , for vectors  $\mathbf{H}$  in the  $(hOl)$  plane of the reciprocal lattice. They determined the  $\mathbf{u}_\kappa$  by least squares refinement of starting values obtained from the way in which the atoms move at the phase transition. We have used their results to derive the sign of each  $G(\mathbf{H})$  and have evaluated  $D(\mathbf{r})$  in projection on the  $xz$  plane. In this instance eq. (1) reduces to

$$D(xz) = \frac{1}{A} \sum_{hl} G(hOl) \cos 2\pi \frac{hx}{a} \sin 2\pi \frac{lz}{c} \quad (3)$$

where the sum involves only terms for which  $h + l$  is even. Figure 1 shows the structure of  $\text{ND}_4\text{D}_2\text{PO}_4$  in projection. To obtain that of  $\text{KD}_2\text{PO}_4$  a potassium atom is placed at the site  $N$ . Figure 2 is a map of  $D(xz)$  in the unique area, the point  $Q$  and the lines  $Qx$ ,  $Qz$  correspond in figures 1 and 2, and atomic sites are similarly identified in both. Negative values of  $D(xz)$  are denoted by dotted lines, positive values by full lines, and contours are drawn at  $\pm 5, 10, 15, 25$  and  $40$  units (arbitrary scale). The origin  $Q$  and the point  $D_1$  are centres of antisymmetry,  $Qz$  is a line of symmetry and  $Qx$  a line of antisymmetry in figure 2. The function  $D(xz)$  shows the expected features, in particu-

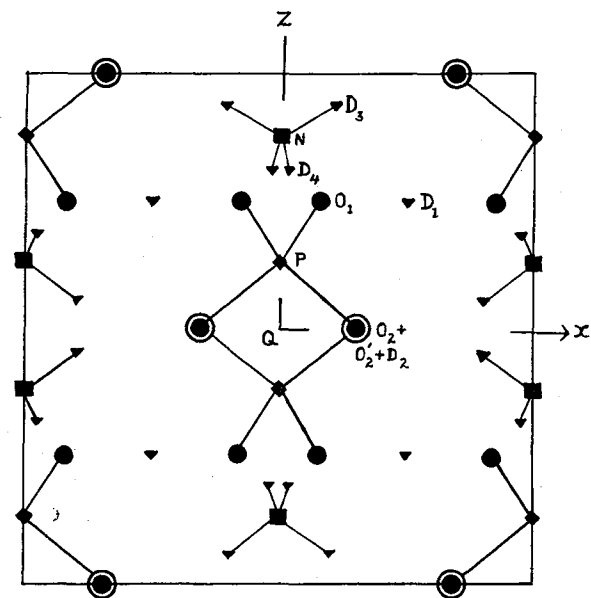


FIG. 1. — Structure of  $\text{ND}_4\text{D}_2\text{PO}_4$  in projection on the  $xz$  plane.

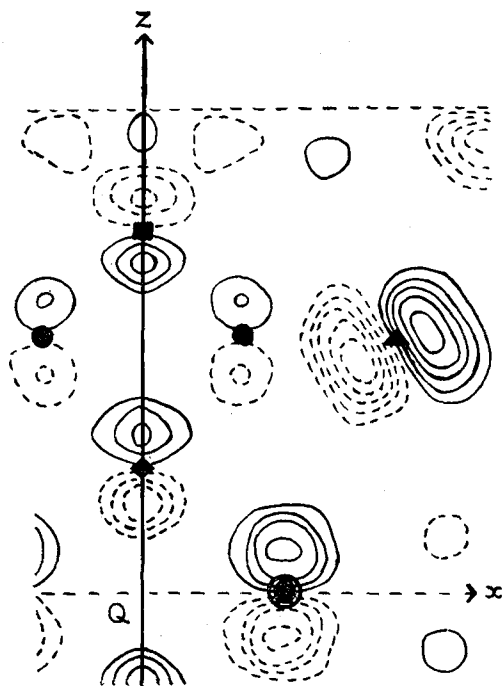


FIG. 2. — Map of  $D(xz)$  for the ferroelectric mode of  $\text{KD}_2\text{PO}_4$ .

lar it confirms that  $\mathbf{u}_D$  is not directed along the hydrogen bond, but at an angle of  $22^\circ$  to it. Values of  $\mathbf{u}_\kappa$  are consistent, within experimental error, with the anticipated symmetry of the mode ( $\Gamma_4$ , in the notation of Montgomery [4]). Numerical values given in Table I have been scaled to make  $u_D = 0.2 \text{ \AA}$ .

TABLE I

$\kappa$	K	P	$O_1$	$O_2$	$D_1$	$D_2$
$(u_\kappa)_x$	—	—	0	?	0.185	—
$(u_\kappa)_z$	-0.046	0.037	0.013	0.013	0.070	0.070

Entries indicated by a dash are zero by symmetry. The value of  $(u_\kappa)_x$  for  $\kappa = O_2$  is, we believe, indeterminate (but see [3]) because atoms  $O_2$  and  $O'_2$  so nearly coincide in projection, and the corresponding values of  $(u_\kappa)_x$  are equal and opposite by symmetry. Our results do not satisfy the condition

$$\sum_{\kappa} m_{\kappa}(u_{\kappa})_z = 0 \tag{4}$$

where the sum is over the atoms in one unit cell, by an amount which lies outside the limit of error. This is to be expected since the measurements do not correspond exactly to  $q = 0$ , and therefore allow an « acoustic contribution » to the optic mode. Otherwise our results agree well with those of Skalyo *et al.* [3].

The measurements of Meister *et al.* [5] on  $\text{ND}_4\text{D}_2\text{PO}_4$  have been extended by us to give a total of thirty six independent values of  $|G(\mathbf{H} - \mathbf{q})|$ . Scattering by the anti-ferroelectric mode occurs at points  $(hkl)$  for which  $h + l$  is odd, referred to the body-centred tetragonal unit cell. As before, measurements are confined to the plane  $k = 0$ . Eq. (1) reduces in this instance to

$$D(xz) = \frac{1}{A} \sum_{hl} G(h0l) \sin 2\pi \frac{hx}{a} \sin 2\pi \frac{lz}{c} \tag{5}$$

Signs were calculated using displacements for  $\text{ND}_4$  and for P given by the (incomplete) crystal structure determination of Keeling and Pepinsky [6], while trying various possibilities for the displacements of the deuterium atoms in the hydrogen bonds. Alternate calculations of  $G(h0l)$  and  $D(xz)$  were then made as in a conventional crystal structure analysis. Best

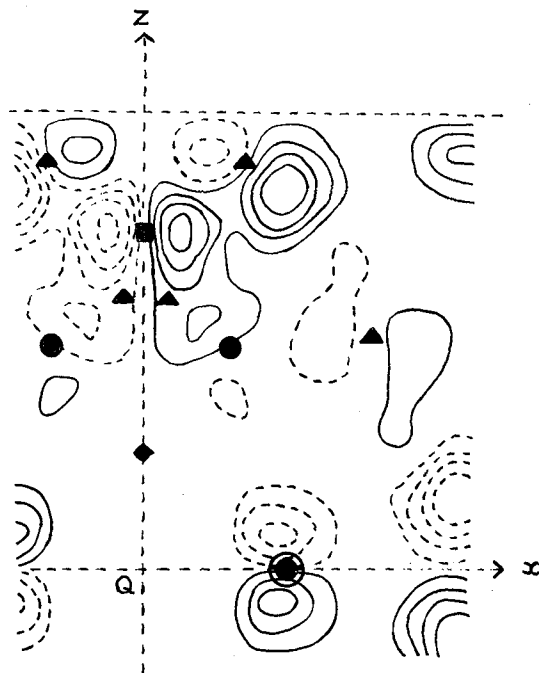


FIG. 3. — Map of  $D(xz)$  for the antiferroelectric mode of  $\text{ND}_4\text{D}_2\text{PO}_4$ .

agreement between calculated and observed values of  $G^2(hOl)$  corresponded to the map of  $D(xz)$  shown in figure 3. Clearly the relative displacement of  $D_1$  in the hydrogen bond is too small to be appropriate for an ordering mode. The value of

$$R = \frac{\sum |G_c^2 - G_0^2|}{\sum G_c^2}$$

is 0.39, and although this is as good as was obtained for  $KD_2PO_4$ , it is possible that our solution of the phase problem is an incorrect one. Therefore we shall

not speculate (in print) on the possible significance of this result, or tabulate the values of  $u_k$  deduced from figure 3. It is worth remarking that there are thirteen non-zero parameters allowed by the symmetry of  $D(xz)$  and in this instance the expected symmetry of the mode,  $M_{34}$ , imposes no further restrictions [4]. One parameter is not determinable from the projection, for the same reason as before.

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