

STRUCTURE OF DEUTERATED KDP CRYSTAL : DEUTERIUM CONCENTRATION DETERMINATION

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Résumé. — Nous avons effectué les mesures des paramètres de la maille élémentaire et de la température de transition T_c de plusieurs cristaux de phosphate de potassium deutérés avec un pourcentage c variable de deutérium 76-96 %. Il a été démontré que le paramètre a_0 (mesuré à 22 °C) et T_c ont une variation linéaire en fonction de la concentration en deutérium. Ces relations sont les suivantes :

$$\begin{aligned} T_c &= 123 + 106 x, \text{ }^\circ\text{K} \\ a_0 &= 7,452\ 39 + 1,759 \times 10^{-2} x, \text{ \AA} \quad \text{où } x = D/(D + H). \end{aligned}$$

Abstract. — Measurements of the structure-cell parameters and ferroelectric Curie temperature, T_c , of a number of tetragonal potassium dideuterium phosphate crystals, with deuterium contents covering range 76-96 %, have been conducted. It has been demonstrated that both the a_0 structure-cell parameter (measured at 22 °C) and T_c exhibit a linear dependence with deuterium content. The relationship between these parameters being established as,

$$\begin{aligned} T_c &= 123 + 106 x, \text{ }^\circ\text{K} \\ a_0 &= 7.452\ 39 + 1.759 \times 10^{-2} x, \text{ \AA} \quad \text{where } x = D/(D + H). \end{aligned}$$

Introduction. — Laser radiation is conventionally controlled by an electro-optic Pockels cell. The fundamental requirements of a material suitable for use in such a cell are that it exhibits a linear electro-optic effect, has high optical transmittance and an operationally low half-wave voltage. This latter parameter is related directly to the electro-optic coefficients of the material.

Crystals of the tetragonal form of potassium dideuterium phosphate, KD_2PO_4 , have been shown to satisfy these requirements and furthermore to possess a high relevant electro-optic coefficient, twice that of KH_2PO_4 at room temperature [1]. Such crystals are conventionally grown from solutions of heavy water by the falling temperature technique. To exploit fully the large electro-optic coefficient it is desirable that highly deuterated crystals be grown. It is important in the assessment of the crystals to be able to determine with adequate precision, say $\pm 2\%$, their deuterium contents. Within our experience, fully deuterated crystals grow in the monoclinic form.

The similarity of KH_2PO_4 and KD_2PO_4 makes it impracticable to attempt to distinguish between these two materials by their chemical reactivity. A mass spectrometer analysis will provide a direct estimation of the composition of the crystals, but not with sufficient precision [2]. Certain physical properties of this structure are known to be dependent on deuterium content. For example, the ferroelectric Curie temperature, T_c , increases from 123 °K for KH_2PO_4 to a value in excess of 220 °K for a highly deuterated crystal [3]. The results of a preliminary examination have also revealed that the a_0 tetragonal structure-cell parameter is dependent on the degree of deuteration.

The primary aim of this investigation was to establish whether there exists a correlation between a_0 , T_c

and the deuterium content of the crystals which could be exploited as an analytical facility.

Results. — The room temperature lattice parameters of the crystals were determined by the X-ray multiple diffraction method. For a description of this method the reader is referred to Isherwood and Wallace [4], Isherwood [5]. This technique was chosen for two main reasons, (i) the high available precision, and (ii) that measurements could be conducted non-destructively on single crystals. Attempts to use the more conventional powder X-ray diffraction methods proved impracticable because of the hydrogen-deuterium exchange with the atmosphere which occurs and which is accelerated when the surface area of the crystal is increased by grinding into the required fine powder.

To remove any damage induced by cutting and polishing and any surface layer which may have been subject to a hydrogen-deuterium exchange the crystals were all heavily etched in D_2O . The effect of exchange at the surface was assessed by monitoring the lattice parameter of a crystal over a period of five days exposure to the atmosphere. Although an obvious surface reaction had occurred no change in lattice parameter was detected. It has been demonstrated that the hydrogen-deuterium exchange is accompanied by a degradation of the crystal structure. As has been previously stated the multiple diffraction method is applicable specifically to the study of single crystals and, therefore, the recorded diffraction patterns will contain information relating essentially to the undistorted crystal matrix. No attempt was made to isolate the crystal from the atmosphere during the period of examination.

The correlation obtained between the two parameters a_0 and T_c for the range of crystal studied is

displayed graphically in figure 1. To a good approximation there is a linear dependence between a_0 and T_c . The corollary of this finding is that both a_0 and T_c exhibit the same functional dependence with deuterium content, expressed as the atomic ratio $D/(D + H)$.

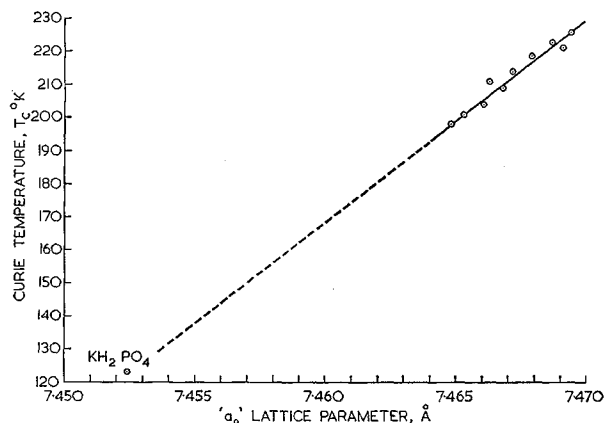


FIG. 1. — Relationship between « a_0 » lattice parameter and Curie temperature for tetragonal $K(D, H)_2PO_4$.

The results of Kaminow [2] would indicate a linear dependence between T_c and $D/(D + H)$ concentration of the crystals. If T_c and $D/(D + H)$ are so related, then it follows that a_0 is also related linearly with $D/(D + H)$. In order to specify the dependence between a_0 and $D/(D + H)$ two calibration points are necessary. In the first instance these were taken as the a_0 parameter of KH_2PO_4 i. e. $D/(D + H) = 0$, and that of a crystal reputedly of 95 % deuteration. The estimate of deuterium contents of the crystal examined from measurements of their a_0 and T_c parameters are tabulated in Table I. Also contained in Table I are the $D/(D + H)$

TABLE I
Deuterium content,
 $D/D + H$ expressed as percentage

Crystal number	Lattice parameter	Curie temp.	H-O-D
1	95	92	—
2	88	90	—
3	71	70.5	—
4	73.5	73	—
5	80.5	81	83
6	79	82.5	—
7	84	85	—
8	78	76	—
9	92.5	94	94
10	96.5	96.5	—

estimates evaluated from the $H-O-D$ infra-red absorption band ($3\ 370\text{ cm}^{-1}$) recorded when the crystals were dissolved in D_2O . Details of these measurements will be published at a later date.

In the three methods of assessment adopted various assumptions were made regarding the dependence of the measured parameters with $D/(D + H)$. These, and the chosen calibration standards, would now appear to be vindicated by the consistency of the $D/(D + H)$ estimates made on the basis of these assumptions. It is concluded, therefore, that both the tetragonal a_0 structure-cell parameter (measured at room temperature, $22\text{ }^\circ\text{C}$) and the ferroelectric Curie temperature, T_c , are linearly dependent on the deuterium content. The relationships between these parameters being established as,

$$T_c = 123 + 106x, \text{ }^\circ\text{K}$$

$$a_0 = 7.452\ 39 + 1.759 \times 10^{-2}x, \text{ \AA}$$

where $x = D/(D + H)$. These results indicate that a fully deuterated crystal, KD_2PO_4 , would exhibit the following parameters,

$$a_0 = 7.469\ 98\ \text{\AA} \quad \text{and} \quad T_c = 229\text{ }^\circ\text{K}.$$

No correlation was established between deuterium content and the c_0 parameter of the tetragonal cell. It is significant, however, that all the deuterated crystals have c_0 parameters which are slightly greater than that of KH_2PO_4 , $c_0 = 6.976\ 56 \pm 0.000\ 03\ \text{\AA}$. Values ranging between $6.978\ 87\ \text{\AA}$ and $6.976\ 65\ \text{\AA}$ have been determined for these crystals. It would appear that any isotope effect on c_0 is not only very small, but is being masked by some other phenomenon, the most likely of which is a variation of the « crystal perfection ». This may be as a result of, for example, impurity segregation on the c -face or faulting of the structure.

It has also been established that there is a partition of hydrogen between the solution and crystals of the tetragonal form of approximately 1.5 : 1, favouring the crystal. Crystals of the monoclinic species grow with a deuterium content closer to that of the solution.

Results of investigations conducted on the monoclinic form of KD_2PO_4 will be reported in a future publication. These will include a precision determination of the parameters of the monoclinic structure-cell and observations on the transformation to the tetragonal phase on exposure to the atmosphere.

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