

FAR INFRARED OPTICAL PROPERTIES OF ADP

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ABSTRACT: The results of infrared and far infrared reflectivity measurements on $\text{NH}_4\text{H}_2\text{PO}_4$ (ammonium dihydrogen phosphate) crystals are presented. The infrared active TO, the associated LO-phonon frequencies and the dielectric functions for both $E \parallel c$ and $E \perp c$ were determined from a four parameter model and fitting procedure. Also group theoretical analysis of the D_2^4 space group of this compound was done.

1. INTRODUCTION

ADP ($\text{NH}_4\text{H}_2\text{PO}_4$) is an optically transparent uniaxial crystal which exhibits anisotropic and nonlinear optical properties.

At the temperature of 148K, ADP undergoes a second order transition of phase. Above this temperature ADP is in a paraelectric phase with the space group D_{2d}^{12} ($I\bar{4}2d$). Below this temperature ADP has another space group - D_2^4 ($P2_12_12_1$) showing antiferroelectric properties.

ADP also exhibits piezoelectric properties and has been extensively used for ultrasonic transducers.

The polarized reflection spectra of ADP at 300 K have been reported using a grating spectrometer [1]. But a proper numerical analysis of the experimental data has not yet been done.

In this work infrared and far infrared optical properties of single crystal ADP were reinvestigated using a more accurate Fourier spectrometer. Optical parameters were calculated for the first time for this material using a fitting procedure.

2. EXPERIMENTAL

Single crystals of ADP were made from water solution using a standard technique. They had a very smooth surface so they did not need to be polished before the reflectivity measurements were made.

Near normal incidence, room temperature polarized far infrared reflectivity measurements were made in the range 40-400 cm^{-1} using a Beckmann FS720 Fourier spectrometer, while infrared reflectivity data in the range 200-2000 cm^{-1} were obtained using a Perkin Elmer 457 spectrophotometer.

In Fig. 1a, 1b and 2a, 2b are given experimental reflectivity curves, with the squares, for $E \parallel c$ and $E \perp c$ respectively, versus wavenumber in the infrared (600-2000 cm^{-1}) and far infrared (30-600 cm^{-1}) range. The solid lines were calculated using the four parameter model introduced by Gervais and Piriou /2/.

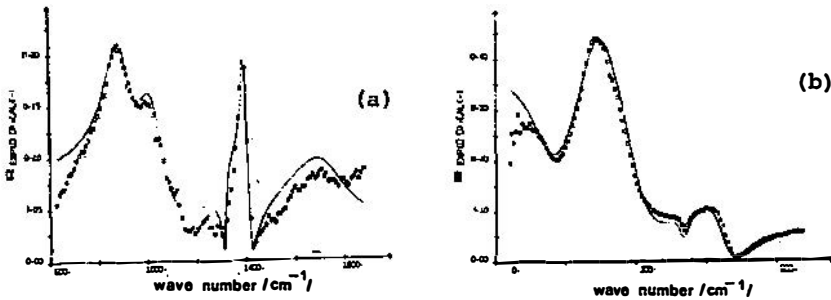


Fig. 1. Experimental infrared (a) and far infrared (b) reflectivity data versus wavenumber (represented as squares) for $E \parallel c$. The solid lines were calculated using the oscillator parameters given in Table 1.

The factorized form of the dielectric function is:

$$\epsilon = \epsilon' - i\epsilon'' = \epsilon_{\infty} + \sum_j \frac{\omega_{jLO}^2}{\omega_{jTO}^2 - \omega^2 + i\gamma_{jLO}\omega} - \sum_j \frac{\omega_{jLO}^2}{\omega_{jTO}^2 - \omega^2 + i\gamma_{jTO}\omega}$$

where ω_{jTO} , ω_{jLO} , γ_{jTO} and γ_{jLO} are transverse (TO) and longitudinal

(LO) frequencies and damping factors respectively.

The values of these optical parameters were obtained and are given in Table 1 for $E//c$ and Table 2 for $E \perp c$ respectively, where ϵ_0 and ϵ_∞ represent the "low frequency" and "high frequency" contribution to the dielectric parameter.

The change of real ($\text{Re}(\text{EPS})$, represented by a solid line) and imaginary ($\text{Im}(\text{EPS})$, represented by a broken line) parts of the complex dielectric function for $E//c$ and $E \perp c$ in the infrared and far infrared ranges are given in Figs. 3a, 3b and 3c, 3d respectively.

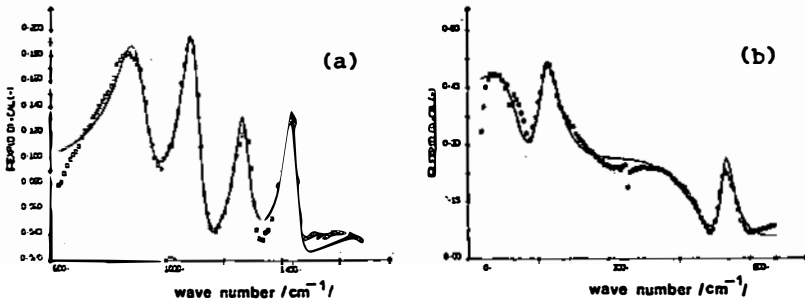


Fig. 2. Experimental infrared (a) and far infra red (b) reflectivity (with the squares) versus wavenumbers for $E \perp c$. The solid lines were calculated using the oscillator parameters given in Table 1.

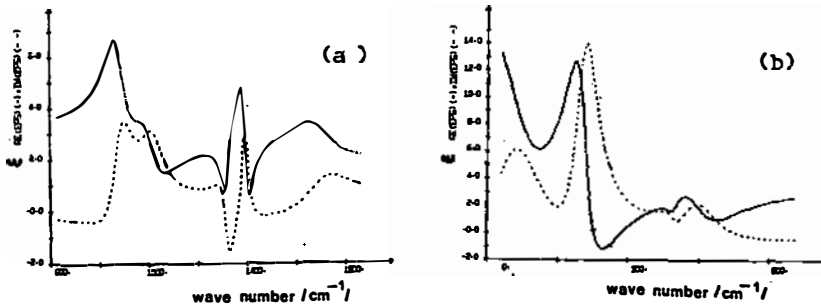


Fig. 3. (a) and (b) .The change of real ($\text{Re}(\text{EPS})$, represented by a solid line) and imaginary ($\text{Im}(\text{EPS})$, represented by a broken line) parts of the complex dielectric function for $E//c$.

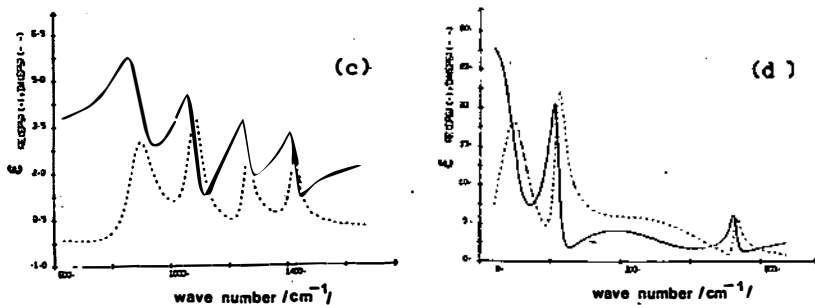


Fig. 3 (c) and (d). The change of real ($\text{Re}(\text{EPS})$, represented by a solid line) and imaginary ($\text{Im}(\text{EPS})$, represented by a broken line) parts of the complex dielectric function for $E \perp c$, in the infra red and far infrared ranges.

Table 1

	$\omega_{\text{TO}} (\text{cm}^{-1})$	$\gamma_{\text{TO}} (\text{cm}^{-1})$	$\omega_{\text{LO}} (\text{cm}^{-1})$	$\gamma_{\text{LO}} (\text{cm}^{-1})$
	110	190	130	95
	205	55	310	100
	398	30	397	20
	457	100	495	55
$E//c$	880	90	913	147
	1015	110	1060	140
$\epsilon_0 = 28$	1318	40	1310	10
	1394	27	1413	18
$\epsilon_\infty = 2.5$	1700	240	1760	350

Table 2

	$\omega_{\text{TO}} (\text{cm}^{-1})$	$\gamma_{\text{TO}} (\text{cm}^{-1})$	$\omega_{\text{LO}} (\text{cm}^{-1})$	$\gamma_{\text{LO}} (\text{cm}^{-1})$
	80	85	130	70
	165	25	190	120
$E \perp c$	425	310	542	65
	545	16	548	150
$\epsilon_0 = 15$	890	100	932	130
	1082	57	1119	75
$\epsilon_\infty = 2.7$	1260	45	1277	70
	1426	38	1445	50

3. DISCUSSION

In this work reflectivity curves for E//c and E⊥c were observed in both infrared and far infrared ranges, for E//c 9 oscillators were detected while for E⊥c 8 oscillators were found. Using transmission measurements at higher frequencies approaching 10000cm^{-1} Murphy and Weiner /3/ observed six more oscillators for E//c and 4 for E⊥c, in the near infrared range. If we include these results with our far infrared and infrared data, we can say that all together 15 oscillators for E//c and 12 for E⊥c were observed.

ADP and KDP (KH_2PO_4) are isomorphous. In the case of KDP factor group analysis D_{2d} reveals that there are 96 optical phonons. Their representation in the centre of the Brillouin zone is:

$$\Gamma = 8A_1 + 10A_2 + 12B_1 + 14B_2 + 26E$$

38 are infrared active ie $13B_2 + 25E$. In addition we should take into account the NH_4^+ ions which possess a tetrahedral symmetry T_d^4 . Their site symmetry in $\text{NH}_4\text{H}_2\text{PO}_4$ is S_4 /4/. For this symmetry there are another 6F infrared modes which have 2 infrared active (B) for E//c and 2 double degenerate infrared modes (2E) for E⊥c. That means that $\text{NH}_4\text{H}_2\text{PO}_4$ should have $13B_2 + 2B = 15$ infrared active modes for E//c and 27E, double degenerated, infrared active modes for E⊥c. Experimentally fewer infrared active modes were observed but those oscillators were very broad. That means that nonregistered oscillators were very close to those which were experimentally observed.

4 REFERENCES

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