LETTER TO THE EDITOR

FOURIER TRANSFORM FAR INFRARED REFLECTION SPECTRA OF PARAELECTRIC KH₂PO₄ AND KD₂PO₄

B. LAVRENČIČ

Institute »Jožef Stefan«, Ljubljana

Abstract: Reflection spectra of KH_2PO_4 and KD_2PO_4 single crystals were interferometrically recorded in the region from 10 cm^{-1} to 100 cm^{-1}. The observed shift of the peak reflectivity in the deuterated sample is discussed in the framework of the soft mode theory of the ferroelectricity.

1. Introduction

There has been recently an increasing interest in the »lattice dynamical« model of ferroelectric crystals as applied to the KH_2PO_4 type hydrogen-bonded ferroelectric crystals[1-4]. In this context, very little is known about the deuterated analogues although they provide answers to some theoretical predictions. One of the methods of studying the low frequency modes in crystals is the use of far infrared spectroscopy. For the lowest region (10 cm^{-1} to 100 cm^{-1}) of measurement there is such a bulk absorption in the specimen that the sample is always thinner than the wavelength of the incident light. The alternative method of studying these modes is the use of the reflection spectroscopy. Here, for a nearly normal reflection, one can compute the shape of the reflectivity. In the case that we have a single damped oscillator one finds[5]

$$\varepsilon(\omega) = \varepsilon(\infty) + \frac{[\varepsilon(0) - \varepsilon(\infty)]\,\omega_o^2}{\omega_o^2 - \omega^2 + i\,2\,\omega\,\Gamma} \,, \tag{1}$$

and

$$R(\omega) = \left| \frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1} \right|^2, \tag{2}$$

where $\varepsilon(\omega)$ is the complex dielectric constant at frequency ω, ω_s and Γ are real and imaginary part of the eigenfrequency of the system, respectively, and $R(\omega)$ is the refectivity at ω.

2. Experiments and results

The reflection spectra were recorded with a Beckman — RIIC FS — 720 Fourier spectrophotometer. The interferogram was stored in an »on-line« computer and then inverted. The angle of incidence was about 15°. Single crystals were oriented along the c-axis which was parallel to the electric field. The spectra were recorded at room temperature only.
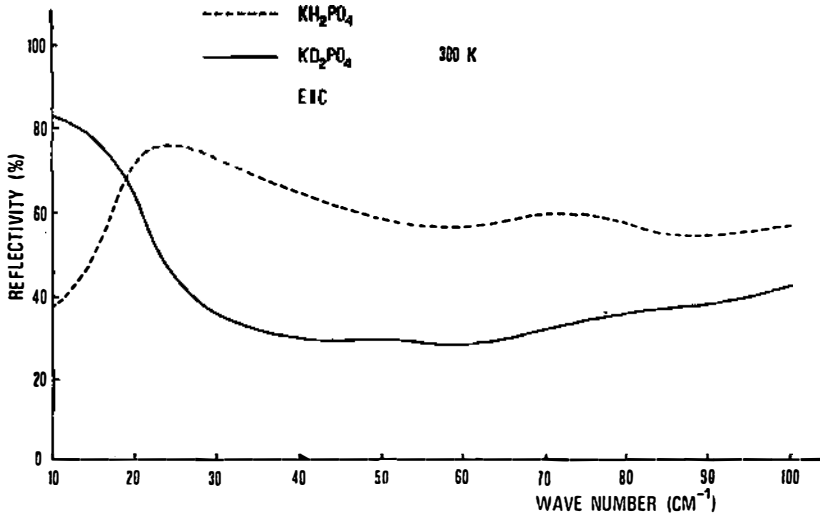

Fig. 1. Smoothed Fourier transform reflection spectra of KH_2PO_4 and KD_2PO_4 single crystals.

The reflection spectra of KH_2PO_4 and KD_2PO_4 agree qualitatively with recent measurements of Kawamura et al.[6]. They used a grating reflection instrument and a large spectral region. It is noticable in the spectrum of KD_2PO_4 that a maximum of reflectivity (approximately maximum of ε'') occurs below 10 cm^{-1} (the lower limit of the instrument). Thus the shift of the peak reflectivity upon deuteration towards lower frequencies clearly demonstrates the importance of a tunneling motion of the protons in the ferroelectric mode of the KH_2PO_4 type crystals, as observed also using Raman[2,3], neutron[7] and Brillouin[8] scattering. The shape of the reflectivity is roughly proportional to the $\varepsilon''(\omega)$ and can be approximated with Debye spectrum (i.e. $\varepsilon(\omega) =$

$= \varepsilon(0)\,\omega\tau/[1 + (\omega\tau)^2]$, where τ is characteristic relaxation time for deuteron interbond motion[9]. The estimated value for τ at room temperature is 10^{-11} s.*

Aknowledgement

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FOURIEROVA DALJNA INFRARDEČA REFLEKSIJSKA SPEKTRA PARAELEKTRIČNIH KH₂PO₄ IN KD₂PO₄

B. LAVRENČIČ

Institut »Jožef Stefan«, Ljubljana

Vsebina

Refleksijska spektra monokristalov KH₂PO₄ in KD₂PO₄ sta bila interferometrično izmerjena v območju od 10 cm⁻¹ do 100 cm⁻¹. Pomik vrha reflektivnosti v devteriranem vzorcu proti nižjim frekvencam je obravnavan v okviru teorije kondenziranega nihanja feroelektrikov.

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* *Note added in proof.* Recently, R. Blinc, J. Stepišnik, M. Jamšek-Vilfan and S. Žumer (J. Chem. Phys., to be published) analysed the deuteron spin lattice relaxation in KD₂PO₄ and have found the τ of the order of magnitude which agrees with our result.