

LATTICE VIBRATIONS IN CRYSTALS OF HYDROXIDES OF ALKALI EARTHS: $\text{Ca}(\text{OH})_2$

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Neutron incoherent inelastic scattering was measured for crystalline $\text{Ca}(\text{OH})_2$ and compared with IR spectroscopy data and with a theoretical model based upon the electrostatic interaction.

1. Introduction

Calcium hydroxide crystallizes in hexagonal system (space group D_{3d}^3). According to Busing and Levy [1], the lattice parameters are: $a = 3.582 \text{ \AA}$, $c = 4.906 \text{ \AA}$. Ca position: (0, 0, 0), O positions: $(1/3, 2/3, 0.234)$ and $(2/3, 1/3, -0.234)$, H positions: $(1/3, 2/3, 0.425)$ and $(2/3, 1/3, -0.425)$. The elementary cell contains one $\text{Ca}(\text{OH})_2$ molecule.

Internal dynamics studies in the calcium hydroxide crystal were performed by the infra-red spectroscopy technique [2], [3], [4], [5], the Raman spectroscopy technique [6], [7], and by neutron inelastic incoherent scattering [8], [9]. Oehler and Günthard [3] presented for $\text{Ca}(\text{OH})_2$ and $\text{Ca}(\text{OD})_2$ not only the IR spectra in the $100 \text{ cm}^{-1} - 14000 \text{ cm}^{-1}$ region, but also an electrostatic model with four adjustable parameters; after fitting to the IR data, dispersion curves for lattice vibrations in the [110] direction were obtained.

In the present paper we calculated the frequency distribution function $g(\omega)$ using the Oehler and Günthard dispersion curves, and performed an experimental check by applying the neutron incoherent inelastic scattering method (IINS).

2. Experimental technique

Measurements were made on the time-of-flight IINS spectrometer [10] installed at the pulsed reactor IBR at Dubna. Neutrons, produced in pulses, passed the moderator — sample distance ($L_1 = 22.30 \text{ m}$) and then, after a 90° scattering, the sample — Zn mono-

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crystal — detector distance ($L_2 = 1.32$ m). The Zn monocrystal fixed the scattered neutron energy at $E' = 5.07$ meV. The incident neutron energy E_0 was selected by the time — of — flight measurement which occurred in a multichannel time analyser connected with the detector. In this way the energy transfer $\Delta E = E_0 - E'$ could be determined.

The polycrystalline $\text{Ca}(\text{OH})_2$ sample (1 mm thickness) was placed in a cryostat in a flat wall aluminium sampleholder. The temperature of measurements was *ca* 80°K.

The energy resolution $\Delta\omega/\omega$ was *ca* 6% [10].

Another IINS measurement, without the Zn monocrystal, but with a beryllium filter in front of the detector, was also made. Its resolution was poorer and amounted to *ca* 15%.

Results were transformed into the $g(\omega)$ function on the basis of the one phonon approximation formula [11], after neglecting (by putting as equal to one) the polarization vector term and the Debye-Waller term.

3. Results and discussion

The results obtained are presented in Fig. 1. The IINS measured $g(\omega)$ function in polycrystalline $\text{Ca}(\text{OH})_2$ has the following peaks: at *ca* 100 cm^{-1} , *ca* 250 cm^{-1} , 310 cm^{-1} , *ca* 340 cm^{-1} , and *ca* 530 cm^{-1} — 550 cm^{-1} . Peaks which appear at frequencies higher than

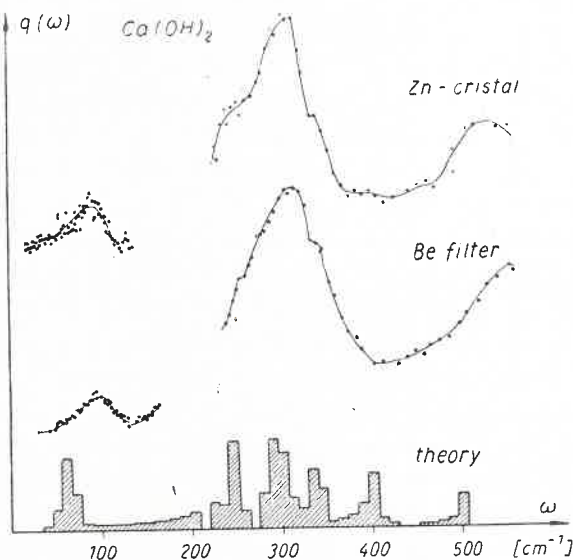


Fig. 1. A comparison of the IINS measured $g(\omega)$ function with the theory [3] based upon an electrostatic model with four IR — fitted parameters

600 cm^{-1} will not be discussed here because of a significant contribution of two phonon effects which deform the shape of the $g(\omega)$ function.

The IINS results obtained by Bajorek [9] give $g(\omega)$ peaks at: *ca* 100 cm^{-1} , *ca* 200 cm^{-1} , 280 cm^{-1} , *ca* 380 cm^{-1} , and *ca* 500 cm^{-1} . In spite of the general similarity of the Bajorek spectra and ours, we must note that Bajorek's values lie systematically lower than ours.

This could be connected with the difference in temperatures; the results [9] were obtained at room temperature whereas our study was made at 80°K.

The IINS results obtained by Safford *et al.* [8] give maxima at 83 cm⁻¹, 247 cm⁻¹, 316 cm⁻¹, and 540 cm⁻¹. These maxima were, however, obtained not by transforming the scattered neutron intensity to the $g(\omega)$ function but by taking the peak positions of the directly measured neutron intensity. As this difference of procedure may be connected with some peak shifts we will not directly compare our data and those of paper [8].

One must also be careful when comparing IINS data and those of optical spectroscopy (at least at low ω values), in view of the fact that the IINS — $g(\omega)$ function contains information from the whole Brillouin zone whereas the usual optical spectroscopy data concern the $q = 0$ region only. It is interesting, on the other hand, to compare with IINS the IR data from the vicinity of the internal OH vibration at 3644 cm⁻¹. This comparison [4] [5] is based upon the assumption that the satellite peaks of the 3644 cm⁻¹ line are caused by combination vibrations: 3644 cm⁻¹ \mp lattice modes. If we accept this assumption and take the mean values of differences between the central 3644 cm⁻¹ line and corresponding satellite peaks at the left and right sides, we obtain the following lattice mode frequencies: 88.5 cm⁻¹, 256 cm⁻¹, 283 cm⁻¹, 319 cm⁻¹, and 545 cm⁻¹. It should be pointed out that these values are not limited to the $q = 0$ region but concern, similarly as neutron data, the whole Brillouin zone in view of the combined excitation character: OH vibron \mp phonon.

A similar interpretation of IR data was also made on the basis of paper [3].

All results which may be directly compared, *i.e.* the IINS data which were transformed to $g(\omega)$ function and the IR data connected with two-quasiparticles absorption, are assembled in Table I.

TABLE I

A comparison of frequency distribution peaks in Ca(OH)₂ obtained in various works

This work IINS temp. 80°K (cm ⁻¹)	Bajorek [7] IINS room temp. (cm ⁻¹)	Busing <i>et al.</i> [4] IR room temp. (cm ⁻¹)	Oehler <i>et al.</i> [3] IR room temp. (cm ⁻¹)
ca 100	ca 100	98.5	92
ca 250	ca 200 (?)	256	
310	ca 280	283	
ca 340	ca 330	319	300
530-550	ca 500	545	540

We shall now pass to a comparison of the results obtained with the theory. The histogram shown in Fig. 1 represents the theoretical $g(\omega)$ obtained from phonon dispersion curves of paper [3]. As was mentioned in the introduction, these dispersion curves were obtained in [3] on the basis of an electrostatic model with four IR fitted parameters. It seems that the agreement of peak positions is good, in spite of the fact that calculations were made for the [110] direction only. The two facts: *a*) neglecting other crystal directions and *b*) neglecting the polarization factor terms which contain the products of neutron cross-sections with averaged $(\vec{\xi} \cdot \vec{\kappa})^2$, (where $\vec{\xi}$ is the polarization vector and $\vec{\kappa}$ the neutron wave vector transfer)

cause a situation in which it is meaningless to compare intensities, but rather the peak positions.

It should be pointed out that an interpretation which could assign a given vibrational type to a given maximum is rather difficult here because of the great complication of the pattern of dispersion curves in the 200 cm^{-1} — 500 cm^{-1} region. In connection with this fact we may say only that the peak at *ca* 100 cm^{-1} is connected with acoustic phonon branches, that at 250 cm^{-1} is a mixture of phonon states of one acoustic branch and the translatory optic vibrations of the E_g type, the peak at 310 cm^{-1} is a mixture of optic translatory and torsional states of the E_u , A_{1g} , A_{2u} types and the next peaks (340 cm^{-1} , and 530 cm^{-1} — 550 cm^{-1}) are connected with torsional phonons of the E_g and E_u types.

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REFERENCES

- [1] W. R. Busing, H. Levy, *J. Chem. Phys.*, **26**, 563 (1957).
- [2] R. M. Hexter, *J. Opt. Soc. Amer.*, **48**, 770 (1958).
- [3] O. Oehler, Hs. H. Günthard, *J. Chem. Phys.*, **48**, 2036 (1968).
- [4] W. R. Busing, H. W. Morgan, *J. Chem. Phys.*, **28**, 998 (1958).
- [5] R. A. Buchanan, H. H. Caspers, J. Murphy, *Appl. Optics*, **2**, 1147 (1963).
- [6] Z. V. Padanyi, *Solid State Comm.*, **8**, 541 (1970).
- [7] D. Krishnamurti, *Proc. Indian Acad. Sci.*, **A50**, 232 (1959).
- [8] G. Safford, V. Brajovic, H. Boutin, *J. Phys. Chem. Solids*, **24**, 771 (1963).
- [9] A. Bajorek, *Thesis* 1965.
- [10] K. Parliński, M. Sudnik-Hryniewicz, A. Bajorek, J. A. Janik, W. Olejarczyk, *IAEA Conference on Pulsed Neutron Sources*, Dubna 1967, p. 179.
- [11] *Thermal Neutron Scattering*; P. A. Egelstaff ed. Acad. Press, 1965, p. 30.