Bulk Polaritons in $K_2Mg_2(SO_4)_3$ Observed by the ATR-Method

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The bulk polariton modes originating from the lattice vibrations of the SO_4-groups in $K_2Mg_2(SO_4)_3$ have been experimentally studied by means of the ATR (attenuated total reflection) method at room temperature. The comparison of the recorded ATR-spectra with the simulation of the ATR-spectra by an oscillator fit shows a satisfying agreement. An assignment of LO- and TO-frequencies based on the results of the oscillator fit is given.

Introduction

The crystal structure of natural $K_2Mg_2(SO_4)_3$ (langbeinite) has been solved in [1] for the first time. This compound belongs to the space group $P2_13$ at room temperature and therefore the infrared active modes to the species T. An early investigation shows that the spectrum of the fundamental optical phonons in $K_2Mg_2(SO_4)_3$ is devided into two parts [2]. In the low frequency region up to about 650 cm^{-1} there are modes originating from librations and vibrations of the heavy potassium- and magnesium-atoms and SO_4-groups. In the frequency region $1000 \leqq \omega \leqq 1300\ cm^{-1}$ there are lattice vibrations from the SO_4-groups only. The experimental technique that allows for the observation of bulk polaritons by ATR (attenuated total reflection)-spectroscopy has been described earlier in [3–7]. A detailed description is therefore omited. Only important facts are briefly reported. In the case of a polyatomic cubic crystal the dispersion relation of bulk polaritons is given by

$$k_{BP} = \frac{\omega}{c} \sqrt{\varepsilon^{\infty} \prod_{j=1}^{n} \frac{\omega_{Lj}^2 - \omega^2}{\omega_{Tj}^2 - \omega^2}}, \tag{1}$$

see [8, 9]. Equation (1) describes the propagation of undamped bulk polaritons with the wave vector k_{BP} and the frequency ω through the crystal. The index j covers the number of infrared active normal modes, which are in question. ω_{Lj} denotes a longitudinal optical phonon eigenfrequency, ω_{Tj} a transversal optical phonon eigenfrequency and ε^{∞} the dielectric constant above the infrared reststrahlen bands. In accord with the experimental conditions given below the reflectivity $R_{TM}(\alpha, \omega)$ of a transverse magnetic (TM) incident electromagnetic wave as a function of the angle of reflection α and the fre-

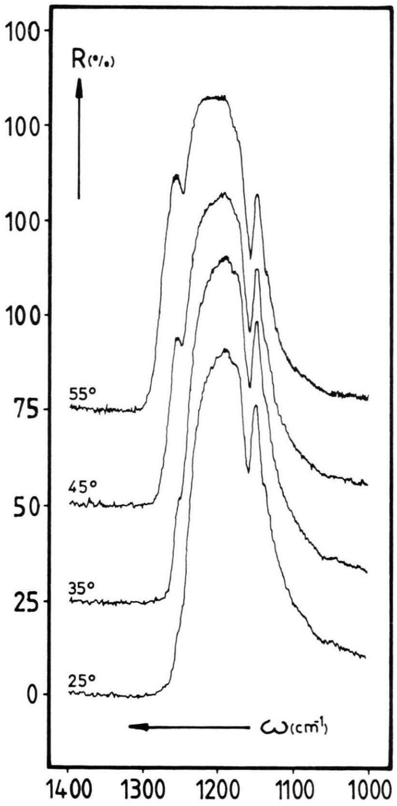

Fig. 1. Infrared reflection spectra of $K_2Mg_2(SO_4)_3$ (langbeinite) recorded by the ATR-technique in TM-geometry, ATR-medium air and different angles of reflection.

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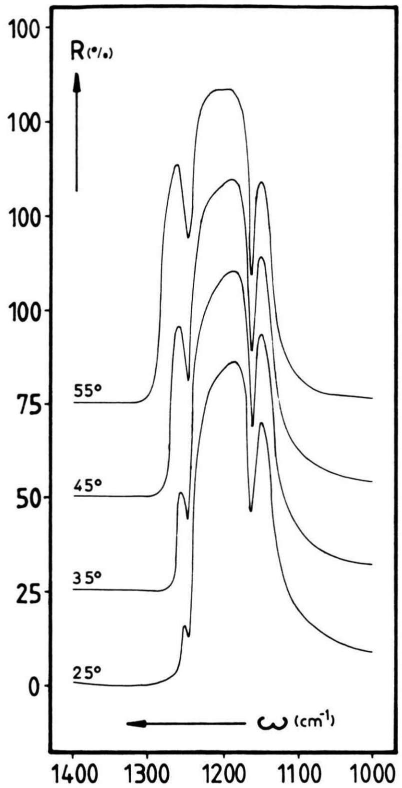

Fig. 2. Infrared reflection spectra of $K_2Mg_2(SO_4)_3$ (langbeinite) for TM-geometry, ATR-medium air and different angles of reflection, simulated by a three oscillator model.

quency ω becomes

$$R_{TM}(\alpha, \omega) = \left| \frac{\sqrt{\varepsilon(\omega)}\; k_{BP} \cos\alpha - n_1 \sqrt{k_{BP}^2 - k_x^2}}{\sqrt{\varepsilon(\omega)}\; k_{BP} \cos\alpha + n_1 \sqrt{k_{BP}^2 - k_x^2}} \right|^2 . \tag{2}$$

The wave vector-component k_x of the incident infrared electromagnetic radiation depends on the angle of reflection α as follows:

$$k_x = \frac{\omega}{c} n_1 \sin\alpha , \tag{3}$$

where n_1 denotes the refractive index of the isotropic ATR-medium over the surface of the sample. If (1) is squared, the frequency dependend dielectric function $\varepsilon(\omega)$ of a cubic polyatomic crystal is obtained:

$$\varepsilon(\omega) = \frac{c^2 k_{BP}^2}{\omega^2} = \varepsilon^{\infty} \prod_{j=1}^{n} \frac{\omega_{Lj}^2 - \omega^2}{\omega_{Tj}^2 - \omega^2} . \tag{4}$$

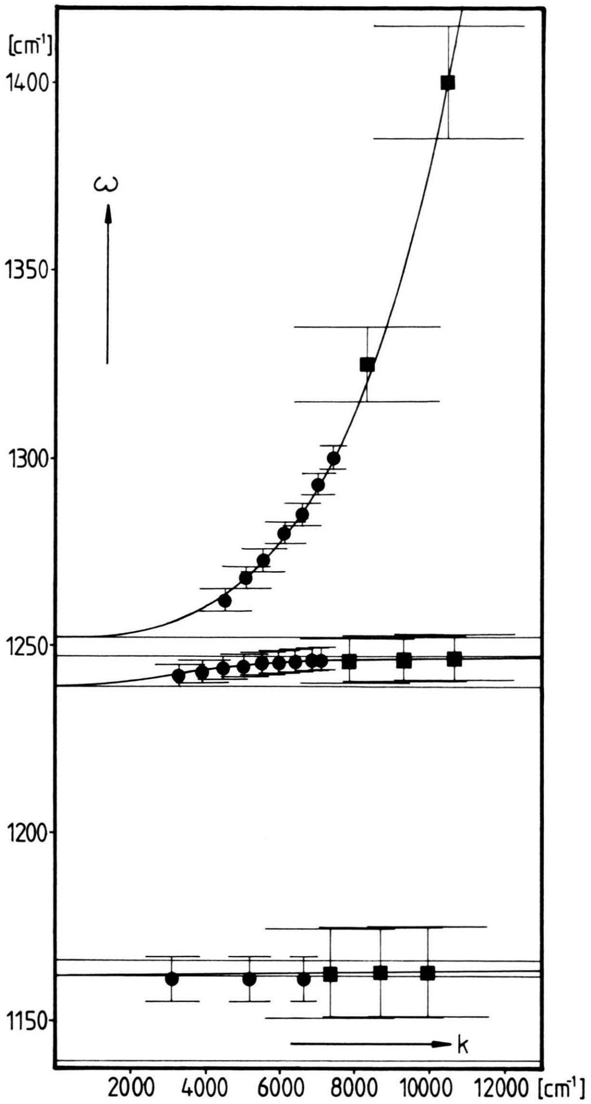

Fig. 3. Turning points of the reflection spectra and dispersion branches $\omega(k)$ of the undamped bulk polaritons originating from the lattice vibrations from the SO_4-groups in $K_2Mg_2(SO_4)_3$ (langbeinite) as calculated by a three oscillator model. Full circles: ATR-medium air. Full squares: ATR-medium KRS-5.

Table 1. Final assignment of LO- and TO-frequencies and damping parameters of $K_2Mg_2(SO_4)_3$ (langbeinite).

j	ω_{Lj} cm^{-1}	ω_{Tj} cm^{-1}	γ_j cm^{-1}
1	1252	1247	10,5
2	1239	1166	8,0
3	1162	1139	10,5

Experiments and Results

It is well known that the edges of the reflection bands in ATR experiments characterize the polariton dispersion branches (i.e. the turning points of the edges), see again [3, 6]. It can easily be shown from (2) that the reflection becomes perfect at a given angle α, a given refractive index n_1 of the ATR-medium and a given frequency ω (i.e. one of the turning points of the edges of the infrared reststrahlen bands) if the condition

$$k_{\mathrm{BP}} = k_x \tag{5}$$

is fulfilled. All experimental data points in Fig. 3 are extrapolated from the recorded spectra in this way. The oscillator fit was done by use of (1), (2), (3) and (4) by finding an assignment of LO- and TO-frequencies and introduction of a damping term $(-i\gamma_j\omega)$ in the numerator and denominator of (1) and (4), respectively. The sample of $K_2Mg_2(SO_4)_3$ was a plate ($4\times8\times2$ mm) of natural langbeinite and polished with diamond paste. The experimental arrangement was the following: The electric vector of the infrared radiation was polarized in the plane of incidence (known as TM-geometry), the ATR-mediums were air ($n_1 = 1.00$) and a KRS-5-hemicylinder ($n_1 = 2.38$), the angles of reflection were varied with an ATR-unit (Beckman ATR UNIT TR 5) in the range from 25 to 65 degrees, a grating spectrophotometer (Perkin Elmer 580 B) and a resolution of 2.3 cm^{-1} was used. The sample and the ATR-medium in the experiments had direct contact. The reflectivity was quantitatively measured by using a surface mirror.

Figure 1 shows a typical series of ATR-spectra recorded for different angles and the ATR-medium air over the surface of the sample. The dispersion branches in question originate from the lattice vibrations of the SO_4-groups in $K_2Mg_2(SO_4)_3$. The results of the classical oscillator fit by using three infrared active oscillators are represented in Figure 2. The comparison of the recorded ATR-spectra from Fig. 1 with the simulated ATR-spectra from Fig. 2 shows a satisfying agreement. The final assignment of the LO- and TO-frequencies with the damping parameters γ_j of the best fit are given in Table 1. The used value of ε^∞ was 2.25. Figure 3 shows the measured dispersion branches (data points) of the undamped bulk polaritons in $K_2Mg_2(SO_4)_3$ and the calculated branches (full curve), using (1), the frequencies given in Table 1 and the value of ε^∞ given above. The agreement is again satisfactory. These results give rise to the conclusion that three infrared active optical phonons characterize the spectrum of $K_2Mg_2(SO_4)_3$ in the frequency region $1000 \leqq \omega \leqq 1300$ cm^{-1}.

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[1] A. Zemann and J. Zemann, Acta Cryst. **10,** 409 (1957).
[2] H. Moenke, Jenaer Jb. **II,** 361 (1959).
[3] R. Claus, L. Merten, and J. Brandmüller, Springer Tracts in Mod. Physics **75,** 178 (1975).
[4] H. J. Falge, A. Otto, and W. Sohler, Phys. Stat. Sol. (b) **63,** 259 (1974).
[5] W. Nitsch, H. J. Falge, and R. Claus, Z. Naturforsch. **29a,** 1011 (1974).
[6] G. Borstel, H. J. Falge, and A. Otto, Springer Tracts in Mod. Physics **74,** 107 (1974).
[7] E. Schuller, H. J. Falge, and G. Borstel, Phys. Stat. Sol. (b) **80,** 109 (1977).
[8] A. S. Barker, Phys. Rev. **136,** 1290 (1964).
[9] R. Claus, Phys. Stat. Sol. (b) **100,** 9 (1980).