Observation of Local Mode Polaritons by Frustrated Total Reflection

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It is shown that local modes due to C^{13}- and N^{15}-Isotopes in their natural abundances of 1.12% and 0.36% in $K_3Cu(CN)_4$ can be observed by the frustrated total reflection technique (FTR) in spite of almost vanishing mode strengths. The observation is made possible by the dispersion of the polariton branches which reduces the reflectivity in the resonance region.

Introduction

The observation of local mode polaritons due to C^{13}- and N^{15}-isotopes in $K_3Cu(CN)_4$ has been reported before by the authors [1–3]. The experimental technique there used for detection was Raman scattering. It could be shown that strong interaction takes place between polaritons originating from the host lattice and isotopic vibrational modes due to localized $^{13}C{\equiv}^{14}N$ and $^{12}C{\equiv}^{15}N$ oscillators in a region where energy ($\hbar\,\omega$) and canonical momentum ($\hbar\,\boldsymbol{k}$) of the excitations become of the same order of magnitude. A condition for this sort of resonance to take place turned out to be a minimum concentration of the impurities which results in average distances between the defects smaller than the polariton wave lengths in the host lattice. The impurity distribution then can be treated as continuous in the electromagnetic wave picture. It is well known [4] that the mode strength S_k of a polar lattice wave is directly related to the frequency splitting of the transverse (ω_T) and longitudinal (ω_L) mode components as follows

$$S_k = (\omega_{Lk}^2 - \omega_{Tk}^2)\,\frac{\varepsilon_\infty}{\omega_{Tk}^2} \prod_{\substack{j=1\\ j\neq k}}^{n} \frac{\omega_{Lj}^2 - \omega_{Tk}^2}{\omega_{Tj}^2 - \omega_{Tk}^2}\,. \tag{1}$$

The mode strength determining the intensity in an infrared (IR) reflection-spectrum thus vanishes for $\omega_{Lk} = \omega_{Tk}$. The number of modes $j = 1, \ldots, n$ in (1) is that for a principal direction of the crystal in question. By fitting the polariton branches experimentally determined from the Raman spectra [2,3] the authors could earlier derive mode strengths of the localized oscillators corresponding to TO – LO-splittings of the order 0.05 cm^{-1} which was well below the resolution of the spectrometer. The oscillator strengths were too small to allow a direct observation by IR-reflection experiments. We shall show, however, that this situation is drastically changed in FTR-reflection experiments because of the dispersion of the transverse localized polariton branches.

Experiments and Discussion

An experimental technique allowing the observation of bulk polaritons by FTR-spectroscopy has first been shown two years ago [5,6].

The FTR hemicylinder in our experiments had direct contact with the sample and the magnetic polarization of the incident and reflected ray, respectively, was arranged perpendicular to the plane of incidence. This has become known as the transverse magnetic (TM) reflection technique. A comprehensive description of the method has been given by Refs. [4,7]. We therefore omit a review of further details. Figure 1 shows the dispersion branches of the E-type polaritons. From higher to lower frequencies the interpretation of the energy levels is as follows: 1) A_1(LO) 2094 cm^{-1}, 2) E(LO) 2085 cm^{-1}, 3) A_1(LO) 2077 cm^{-1}, 4) A_1(TO) 3074 cm^{-1}, 5) $^{12}C{\equiv}^{15}N$ impurity mode at 2053 cm^{-1} and 6) $^{13}C{\equiv}^{14}N$ impurity mode at 2040 cm^{-1}. The straigth line A describes the vacuum dispersion of photons $\omega = c\,k$ and the line B gives the limit of observation which in our experiments was determined by the refractive index n' of the KRS5-hemicylinder and a maximum reflection angle $\alpha = 60°$:

$$\omega = \frac{c}{n' \sin\alpha}\, k_x\,. \tag{2}$$

k_x is the wave vector component propagating parallel to the surface of the crystal. The optic axis (z) in turn was parallel to k_x, see [6]. Variation of the reflection angle α leads to records of different spectra corresponding to almost vertical traces indicated by the angles $\alpha = 30°$, 40°, and 50° in Fig. 1. From simple considerations when neglecting damping it follows that the hatched areas in Fig. 1 require

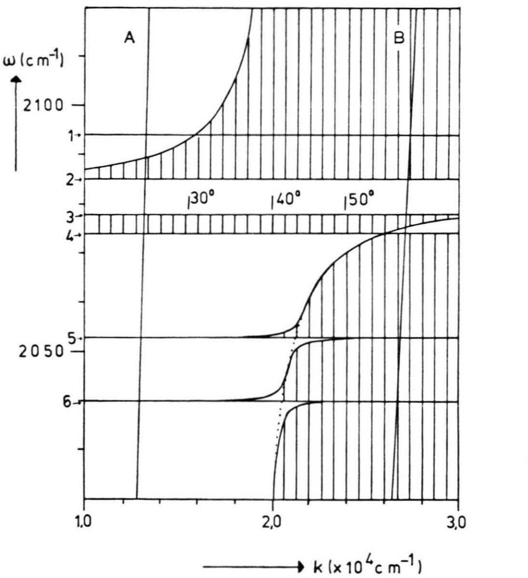

Fig. 1. Dispersion branches of E-type polaritons originating from the host lattice and localized oscillators: $^{12}C \equiv {}^{15}N$ (2053 cm^{-1}) : level 5 and $^{13}C \equiv {}^{14}N$ (2040 cm^{-1}) : level 6. Hatched areas correspond to regions of high reflection. For further explanations see text.

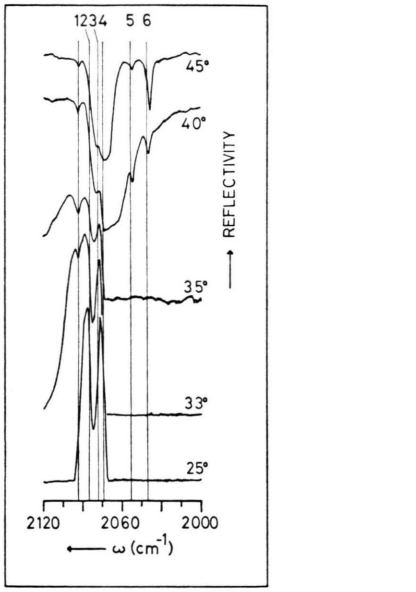

Fig. 2. TM-reflection spectra corresponding to the traces $\alpha = 25°$, $33°$, $35°$, $40°$ and $45°$ in the ω/k-diagram, Fig. 1. The spectra were recorded by the FTR-method, the KRS5-hemicylinder having direct contact with the sample.

complete reflection whereas the crystal appears transparent for photons with energies and momenta in the remaining areas, see again[4, 7].

Different points on the dispersion curves correspond to the turning points of the bands in the spectra. A spectra series of this kind is shown in Figure 2. The traces for $\alpha = 25°$, $33°$ and $35°$ do not show any influence of the localized oscillator modes but only reflection bands originating from the host lattice. For $\alpha = 40°$ and $\alpha = 45°$, however, two dips caused by the two localized oscillators at the energy levels 5) and 6) can easily be identified. The polariton dispersion curve of the unperturbed host lattice has been indicated by a dotted line in Figure 1. Because of mode couplings with the impurity oscillators in the two frequency regions in question the reflectivity is remarcably reduced for traces between $\alpha = 40°$ and $\alpha = 50°$. For traces well above $\alpha = 50°$ the areas become narrower than it would be possible to show in Fig. 1 (horizontal lines!). It is important to note that modes with extremely small but not completely vanishing oscillator strengths in the phonon region thus may be observed in the polariton region. This is of course true also for all others types of polariton modes such as second order polaritons, plasmaritons or magnaritons. Figure 3 correspondingly shows reflection spectra and the ω/k-diagram of A_1-type modes in the high frequency polariton region of $K_3Cu(CN)_4$. In order better to show the analogies between the experiment (left figure) and the calculated dispersion phenomena (right figure) that latter figure has been turned around by an angle of 90° and the (now vertical) k-axis has been calibrated in terms of the reflectance angle α. This allows us directly to identify the spectra to the left from horizontal cuts at the corresponding angle-levels in the right figure. For better orientation one of the turning points of the reflection bands and the corresponding point on the dispersion curves has been indicated by a black square for $\alpha = 47°$. The counted energy levels in the figures are 1) A_1(LO) 2077 cm^{-1}, 2) E(TO) 2080 cm^{-1}, 3) E(LO) 2085 cm^{-1}, and 4) A_1(LO) 2094 cm^{-1}. We want to point out that the determination of the position of the intersection point between the E(LO)-branch at 2085 cm^{-1} and the transverse totally symmetric (A_1-)polariton branch can be determined with an extremely high accuracy: In agreement with the prediction from the hatched total reflection areas in the right figure the

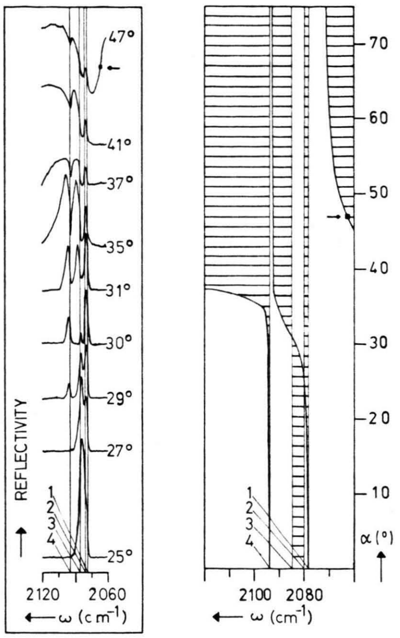

Fig. 3. FTR-reflection spectra (left figure) and dispersion branches (right figure) of the high frequency A_1-polaritons in $K_3Cu(CN)_4$. The right figure has been turned around by 90° compared with Figure 1. The k-axis furthermore is directly calibrated in terms of the reflectance angle α in order easier to allow a comparison with the experimental results. The optical axis is oriented vertical to the surface of the $K_3Cu(CN)_4$ crystal. For further details see text.

reflection band in the $\alpha = 30°$ spectrum lies to the right of the E(LO) frequency in question whereas is has jumped over to the left in the $\alpha = 31°$-spectrum. In order to fit the k-value of this crossing point it is necessary to reduce the TO – LO-splitting of the A_1-phonon pair at 2094 cm^{-1} to 0.1 cm^{-1}. Such a small TO – LO-splitting could not be directly determined in our earlier Raman scattering experiments. We furthermore note that the FTR-reflection experiments allowed an observation of the dispersion branches towards smaller k-values than the Raman scattering experiments made possible when using the red line of a Kr^+-laser (647.1 nm) for excitation.

In agreement with the earlier published light scattering experiments [2, 3] four A_1-resonances may be found in the energy region of the localized modes by FTR. The resolution in the reflection spectra in general, however, was not superior to the earlier experiments.

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