

# Interaction of Isotopic Modes with Polaritons

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Weak phonon modes at 2032.5; 2040; 2046; and 2053  $\text{cm}^{-1}$  in  $\text{K}_3\text{Cu}(\text{CN})_4$  have been assigned to originate from  $^{13}\text{C}\equiv^{14}\text{N}$  and  $^{12}\text{C}\equiv^{15}\text{N}$  vibrations. The assignments have been carried out using measurements at He-temperatures and in aqueous solutions. Furthermore calculations have been used concerning the frequency shifts and relative intensities with respect to the  $^{12}\text{C}\equiv^{14}\text{N}$  vibrations. The coupling of polariton modes associated with the  $A_1$ -phonon at 2074 and the E-phonon at 2080  $\text{cm}^{-1}$  with the isotopic modes has been experimentally investigated. A comparison of calculated dispersion branches with the experimental data has shown that the isotopic modes can not simply be treated as fundamentals because the coupling observed is much weaker than expected from the general polariton dispersion theory for first order phonons.

## Introduction

Interactions between elementary excitations in matter are frequently observed as a resonance splitting of the corresponding dispersion branches  $\omega = \omega(\mathbf{k})$  in a region where the energies and momenta of the excitations are approximately equal. Polaritons representing the interaction between polar optical phonons and photons have first been observed in this way by Henry and Hopfield<sup>1</sup>. The coupled state plasmon-polariton which may exist in the presence of a magnetic field has been observed in the same way by Patel and Slusher<sup>2</sup>. Coupling between polar phonons causes the same behaviour as has been shown by Scott<sup>3</sup>. Extraordinary polaritons caused by the interaction of a polariton with another polar optical phonon also show this behaviour, see Ref. <sup>4</sup> and <sup>5</sup>. The list of examples could easily be continued. In order to show such resonances experimentally an external parameter normally is required allowing the variation of  $\mathbf{k}$  and  $\omega$ . In the four examples cited above these parameters are the scattering angle between the incident and scattered light, the magnetic field, the temperature and the orientation of the wave vector with respect to the optic axis. In the case of polaritons the variation of the scattering angle easily allows investigations in the first Brillouinzone over a  $\mathbf{k}$ -range of approximately one order of magnitude. In suitable materials with modes showing strong dispersion, frequency shifts of more than 100  $\text{cm}^{-1}$  are observed<sup>6,7</sup>. This made it possible to try scattering experiments concerning the coupling between polaritons and other excitations as for instance second order phonon processes. Corresponding results have become known on  $\text{LiNbO}_3$ <sup>8,9</sup>,  $\alpha\text{-HfO}_3$ <sup>10</sup> and  $\text{LiIO}_3$ <sup>11</sup>.

Two early papers concerning resonant crossings in  $\text{K}_3\text{Cu}(\text{CN})_4$  with polaritons involved have been published by Claus<sup>12</sup> and Claus and Schrötter<sup>13</sup>. The lack of any directional dispersion of the magnitude of the resonance splitting caused the authors to reject an interpretation as resonant crossing between two first order branches<sup>12</sup>. An interpretation as coupling with a second order process on the other hand could be based on the fact that for both resonances which were experimentally observed the weak phonon components could be assigned as difference bands with the lowest frequency  $A_1$  and E-phonons in agreement with the selection rules and within an accuracy of  $\pm 2 \text{ cm}^{-1}$  (see also Ref. <sup>14</sup>). Anyhow experiments at He-temperatures which should show a decreasing scattering intensity of the "difference bands" because of the lower population at lower temperatures could not be made at that time. Accordingly some discussion about the origin of the resonances remained<sup>15</sup>. The intention of the present work was to clear up this question definitely. The experiments showed the result that the resonances are neither caused by first nor by second order process but by isotopic impurities due to  $^{13}\text{C}$  and  $^{15}\text{N}$  atoms. The use of better experimental equipment furthermore allowed the observation of a total number of 4 resonances instead of only 2 as reported in the earlier papers.

## Discussion of the Isotopic Modes

In the high frequency region of the phonon spectrum of  $\text{K}_3\text{Cu}(\text{CN})_4$  originating from  $\text{C} \equiv \text{N}$  stretching vibrations, first order phonons have been assigned as<sup>14</sup>: 2094  $\text{cm}^{-1} = A_1$  (LO); 2093  $\text{cm}^{-1} = A_1$  (TO); 2085  $\text{cm}^{-1} = E$  (LO); 2080  $\text{cm}^{-1} = E$



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(TO);  $2077\text{ cm}^{-1} = A_1$  (LO) and  $2074\text{ cm}^{-1} = A_1$  (TO). Furthermore four phonons with scattering cross sections of approximately one order of magnitude less have been observed as  $2053\text{ cm}^{-1} = E$ ;  $2046\text{ cm}^{-1} = A_1$ ;  $2040\text{ cm}^{-1} = E$  and  $2032.5\text{ cm}^{-1} = A_1$ .

According to considerations by Chisler<sup>16</sup> the decrease of the scattering intensity of for instance a difference band at  $2033\text{ cm}^{-1}$  is expected to be more than 90% when the temperature is lowered from 300 K to 50 K. From Ref. <sup>14</sup> it can be seen that such a second order phonon would be expected from  $(2093 - 60)\text{ cm}^{-1}$  where the peak at  $60\text{ cm}^{-1}$  corresponds to the lowest strong  $A_1$ -phonon of the spectrum. The experimental result reproduced in Figure 1, however, shows no decreasing intensity of

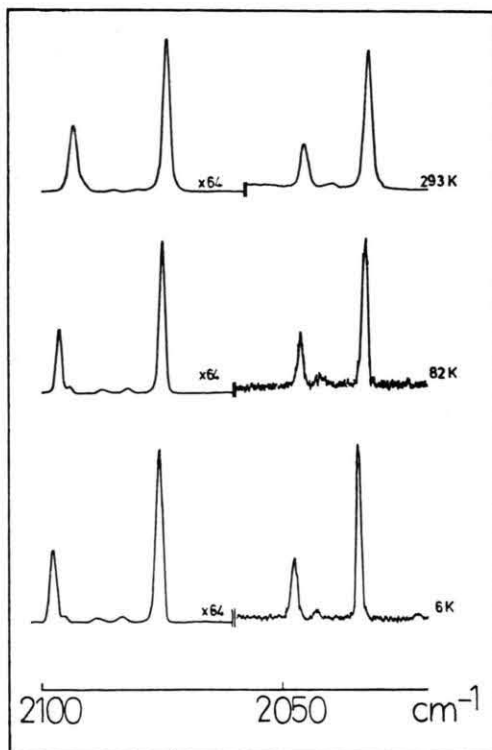


Fig. 1. High frequency phonon spectrum of  $\text{K}_3\text{Cu}(\text{CN})_4$  originating from  $\text{C}\equiv\text{N}$  vibrations recorded at 293, 82 and 6 K. The scattering geometry is  $x(\text{zz})y$ , showing  $A_1$ -type phonons.

the corresponding weak peaks observed in the spectra at 82 K and 6 K. Regarding the group theoretical correlation of the vibrations of a free  $\text{Cu}(\text{CN})_4^{3-}$  ion, a hypothetical  $\text{CuX}_4$ -group and 2 ions in the unit cell of the material belonging to the space group  $R\bar{3}c$  ( $=C_{3v}^6$ ) the result is that

4 internal vibrations of  $A_1$ -type are expected to originate from  $\text{C}\equiv\text{N}$  vibrations. Two of them are easily identified as the stretching vibrations appearing at  $2093$  and  $2074\text{ cm}^{-1}$  as transversal and correspondingly at  $2094$  and  $2077\text{ cm}^{-1}$  as longitudinal modes. The other two, however, correspond to bending modes and as such are expected in the region at about  $300\text{ cm}^{-1}$ . Following the assignment of the fundamentals of the free  $\text{Cu}(\text{CN})_4^{3-}$  ion, given by Jones<sup>18</sup>, there is one vibration of type  $A_1$  and one vibration of type  $F_2$  in the high frequency region. These vibrations are split by site symmetry into 2  $A_1$  and 2  $E$  phonons in the crystal, where each of them may show an LO-TO splitting in addition. Since obviously both interpretations of the  $A_1$ -phonons at  $2032.5$  and  $2046\text{ cm}^{-1}$  as first order and second order process fail, these phonons can alternatively be expected to originate from  $^{13}\text{C}$  and  $^{15}\text{N}$  isotopic impurities i.e. vibrations of  $^{13}\text{C}\equiv^{14}\text{N}$  and  $^{12}\text{C}\equiv^{15}\text{N}$  groups. The situation is analogous for the  $E$ -type modes.

Using a simple two mass oscillator model and taking the Born-Oppenheimer approximation into account; the frequency shifts can easily be calculated from

$$\omega_i/\omega = (\mu/\mu_i)^{1/2},$$

where  $\mu = m_{\text{C}} \cdot m_{\text{N}} / m_{\text{C}} + m_{\text{N}}$  stands for the reduced mass of the oscillator  $^{12}\text{C}\equiv^{14}\text{N}$  and  $\mu_i$  for the reduced masses of the oscillators containing one of the isotopes, respectively. The result is shown in Table 1. A comparison with the experimental data

Tab. 1. Theoretical and experimental data concerning the wave numbers of vibrations originating from  $\text{C}\equiv\text{N}$  groups containing the isotopes  $^{13}\text{C}$  and  $^{15}\text{N}$ , respectively.

	$A_1$ -modes		$E$ -modes	
	theor.	exp.	theor.	exp.
$^{13}\text{C}\equiv^{14}\text{N}$	2030,6	2032,5	2036,5	2040,0
$^{12}\text{C}\equiv^{15}\text{N}$	2042,0	2046,0	2047,8	2053,0
$^{12}\text{C}\equiv^{14}\text{N}$		2074,0		2080,0

shows, that a maximum difference of  $5.2\text{ cm}^{-1}$  is observed in only one case. Regarding the simplicity of the model and the complete neglect of the coupling to the central Cu atom, the agreement is rather satisfying and supports the assignment suggested. In order to confirm the assignment aqueous solutions of  $\text{K}_3\text{Cu}(\text{CN})_4$  have been inspected. The free  $\text{Cu}(\text{CN})_4^{3-}$ -ions should also exhibit vibrations

due to the isotopes. The experiment at least allowed the identification of two weak vibrations of totally symmetric type at 2035 and 2048  $\text{cm}^{-1}$  corresponding to the  $A_1$ -phonons at 2032.5 and 2046  $\text{cm}^{-1}$  of the crystal. The identification of  $F_2$ -type vibrations in the  $I_{||}$ -spectrum is uncertain, see Figure 2.

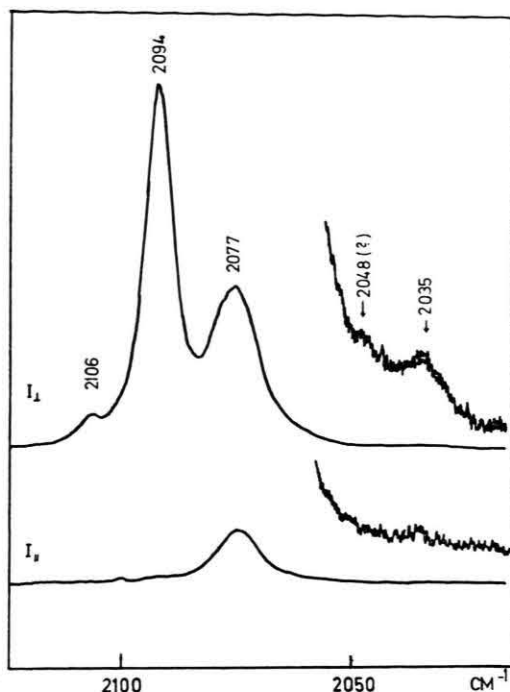


Fig. 2. Vibrational spectrum of the  $\text{Cu}(\text{CN})_4^{3-}$ -ion in an aqueous solution. Spectral slit width = 3  $\text{cm}^{-1}$ .

The relative abundances of the stable carbon and nitrogen isotopes are

$$\begin{aligned} [^{12}\text{C}] &= 98.892\%, & [^{13}\text{C}] &= 1.108\%, \\ [^{14}\text{N}] &= 99.64\%, & [^{15}\text{N}] &= 0.36\%. \end{aligned}$$

One of the four  $\text{C} \equiv \text{N}$  groups of every  $\text{Cu}(\text{CN})_4^{3-}$  ion has its bond parallel to the optic axis of the crystal. Regarding the stretching vibration which leads to the  $A_1$ -phonon at 2074  $\text{cm}^{-1}$  we have a remarkable contribution to the corresponding normal coordinate and thus the Raman tensor elements. The probabilities to find one of the isotopes  $^{15}\text{N}$  or  $^{13}\text{C}$  in such a group are

$$[^{13}\text{C}] = 1.058\%, \quad [^{15}\text{N}] = 0.34\%.$$

These probabilities are somewhat less than the abundances cited above because there will also exist some doubly marked groups:  $^{13}\text{C} \equiv ^{15}\text{N}$ . Because of the very low concentration ( $3.6 \cdot 10^{-5}$ ) the vibra-

tions of these groups could not be recorded in the present work. The scattering intensities of the  $^{13}\text{C}$  and  $^{15}\text{N}$  marked groups should be approximately proportional to their concentrations and thus the ratio of the scattering intensities is expected to be

$$\frac{I(^{13}\text{C} \equiv ^{14}\text{N})}{I(^{12}\text{C} \equiv ^{15}\text{N})} = \frac{[^{13}\text{C}] \cdot [^{14}\text{N}]}{[^{12}\text{C}] \cdot [^{15}\text{N}]} = 3.11.$$

As a matter of fact the experimental result is 3.14 which again supports the assignment of the phonon modes<sup>17</sup>. Finally it should be pointed out that the assignment as isotopic modes has also been proposed by Jones<sup>18</sup>.

### Polariton Scattering Results

Using a near forward scattering technique<sup>19</sup> the polariton spectra of transversal  $E$  and  $A_1$ -type phonons in the high frequency region have been experimentally investigated. Corresponding spectra series have been reproduced in Figs. 3 and 4, respectively.

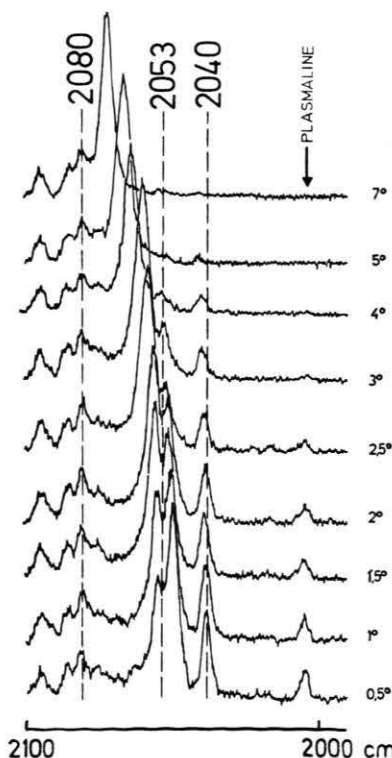


Fig. 3. Spectra series showing the coupling of the polariton associated with the  $E(\text{TO})$ -phonon at 2080  $\text{cm}^{-1}$  in  $\text{K}_3\text{Cu}(\text{CN})_4$  with modes originating from the isotopic impurities  $^{13}\text{C}$  and  $^{15}\text{N}$ . Scattering geometry  $y(xz)y$  for  $\varphi = 0^\circ$ . Scattering plane:  $xy$ . Exciting laser: 647.1 nm, 600 mW. Spectral slit width 3  $\text{cm}^{-1}$ .

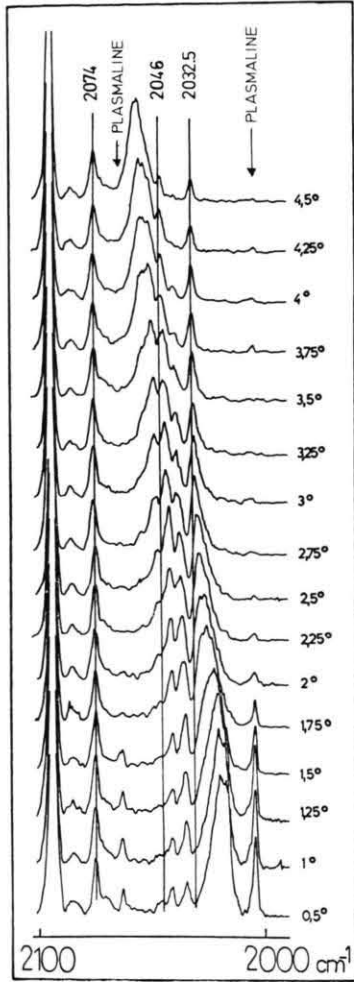


Fig. 4. Spectra series showing the coupling of the polariton associated with the  $A_1(\text{TO})$ -phonon at  $2074 \text{ cm}^{-1}$  with isotopic modes. Scattering geometry:  $x(\text{zz})x$  for  $\varphi=0^\circ$ . Scattering plane:  $xy$ . Exciting laser line =  $647.1 \text{ nm}$ ,  $600 \text{ mW}$ . Spectral slit width:  $2 \text{ cm}^{-1}$ .

As can directly be seen the  $E$ -polariton in Fig. 3 shows two resonances appearing at  $2040$  and  $2053 \text{ cm}^{-1}$ . These wave numbers coincide with those of the two weak modes of  $E$ -type discussed above. The angles given to the right of the scans correspond to the internal scattering angles between incident and scattered photons. The use of the optically isotropic scattering plane  $= xy$  allows the elimination of any directional dispersion effects from the spectra. All polariton modes thus are exactly of twofold degenerate type. Correspondingly the polariton modes in Fig. 4 associated with the  $A_1(\text{TO})$ -phonon at  $2074 \text{ cm}^{-1}$  are exactly of type  $A_1(\text{TO})$ . Also in this case coupling takes place with the isotopic

modes. The positions of the two weak phonons of type  $A_1$  at  $2032.5$  and  $2046 \text{ cm}^{-1}$  have been indicated by vertical lines. The polariton mode, however, also shows resonances with the  $E$ -type modes at  $2040$  and  $2053 \text{ cm}^{-1}$ . This coupling is rather strong at least with the phonon at  $2040 \text{ cm}^{-1}$ . Finally the experimental data indicate a weak resonance with a phonon at  $2024 \text{ cm}^{-1}$  which could not be recorded in the phonon spectra. Note, that thus this sort of experiments involves a rather great factor of amplification which easily can make possible the detection of phonon lines with extremely small cross sections! Using the optically anisotropic scattering plane  $= xz$ ,  $z$  denoting the optic axis, the resonances show an almost identical behaviour. In this case couplings with impurity modes of both types  $A_1$  and  $E$  are expected since, the polariton mode is of mixed type  $A_1 + E$  for arbitrary wave vector directions. It could, however, be shown that the resonances with  $E$ -type modes appearing in Fig. 4 are not caused by misorientations or oblique scattering geometries. Thus we have to assume that the two impurity modes at  $2040$  and  $2053 \text{ cm}^{-1}$  at least in the resonance region also have some  $A_1$ -character. This result is somewhat unexpected because the corresponding phonon spectra did not allow the observation of these modes (see Ref. <sup>14</sup>).

The dispersion curves of  $E$ -type polaritons can be calculated from

$$k^2 c^2 / \omega^2 = \varepsilon_{\perp\infty} \prod_{i=1}^n (\omega_{Li\perp}^2 - \omega^2) / (\omega_{Ti\perp}^2 - \omega^2), \quad (1)$$

and those for  $A_1$ -type polaritons correspondingly from

$$k^2 c^2 / \omega^2 = \varepsilon_{\parallel\infty} \prod_{i=1}^m (\omega_{Li\parallel}^2 - \omega^2) / (\omega_{Ti\parallel}^2 - \omega^2), \quad (2)$$

$L$  and  $T$  referring to longitudinal and transversal  $\perp$  and  $\parallel$  to lattice displacements perpendicular and parallel to the optic axis.  $n$  and  $m$  are the number of  $E$  and  $A_1$ -type modes, respectively. The high frequency dielectric constants  $\varepsilon_{\perp\infty} = 2.35$  and  $\varepsilon_{\parallel\infty} = 2.32$  were calculated from the dispersion of the refractive indices which have been extrapolated to  $2000 \text{ cm}^{-1}$ . Because of the great gap between the low and high frequency phonon spectra of  $\text{K}_3\text{Cu}(\text{CN})_4$ <sup>14</sup> the high frequency region has been treated separately omitting the frequencies of the lower region. This approximation seems to be justified when examining the results in Figs. 5 and 6. The



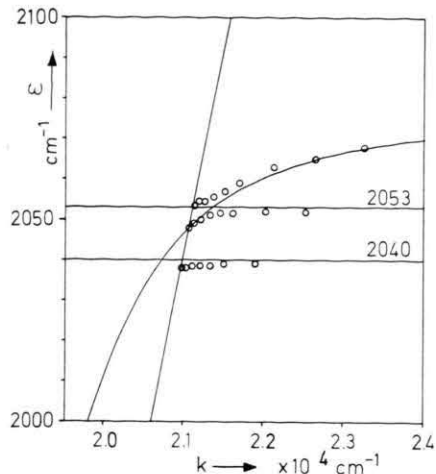


Fig. 5. Dispersion curve and experimental data concerning the  $E$ -polariton. The impurity modes have theoretically been left out of consideration. Scattering geometry:  $y(xz)y$  for  $\varphi=0^\circ$ . Scattering plane  $xz$ . (The data do not directly correspond to the scans of Figure 3!) The nearly vertical straight line indicates the observation limit.

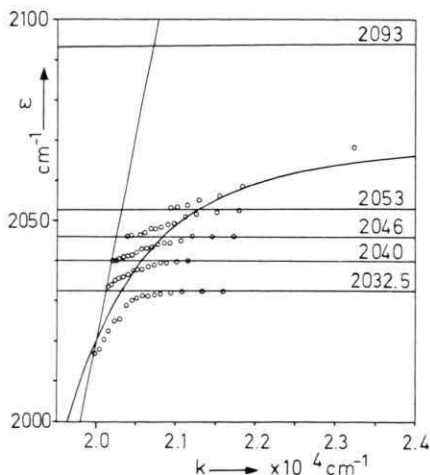


Fig. 6. Dispersion curve and experimental data concerning the  $A_1$ -polariton. The impurity modes have been left out of consideration in the calculation. Scattering geometry:  $y(zz)y$  for  $\varphi=0^\circ$ . Scattering plane:  $xy$ .

dispersion has here been calculated for the  $E$  and  $A_1$ -type polaritons, respectively, without taking the impurity modes into account. The experimental data fit the curves outside the resonance region in both cases and connect the points of maximum resonance very well. The "limiting lines" to the left in the figures determining the maximum frequency shifts observable at straight forward scattering are obtained from the wave vector relation  $\mathbf{k}_i = \mathbf{k}_s + \mathbf{k}$ ,  $\mathbf{k}_i$  and  $\mathbf{k}_s$  standing for the incident and scattered photons (see for instance Ref. <sup>20</sup>).

In order to examine whether the impurity modes can still be regarded as first order phonons or not dispersion branches have been calculated from Eq. (2) taking the  $A_1$ -modes at 2032.5 and 2046  $\text{cm}^{-1}$  into account, Fig. 7, and finally in addition taking

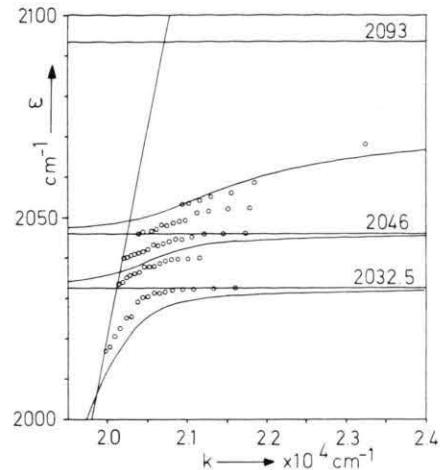


Fig. 7. Experimental data concerning the  $A_1$ -polariton. The dispersion curves have been calculated taking into account only the impurity modes of type  $A_1$  at 2032.5 and 2046  $\text{cm}^{-1}$  in addition to the fundamentals.

into account also the  $E$ -modes at 2040 and 2053  $\text{cm}^{-1}$ , Figure 8. Comparison with the experimental data shows that a satisfactory agreement could not be obtained. The couplings which are experimentally observed obviously are weaker than expected for pure first order modes. This suggests that the modes

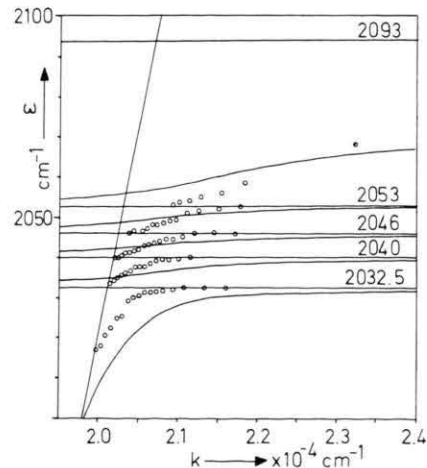


Fig. 8. Experimental data concerning the  $A_1$  polariton. The dispersion curves have been calculated taking into account the two impurity modes of type  $E$  at 2040 and 2053  $\text{cm}^{-1}$  in addition to Figure 7.

will still have the character of localized modes. Numerical calculations using the theory by Ohtaka<sup>21</sup> are in preparation.

In order to support the results obtained on  $K_3Cu(CN)_4$  also the polariton region of  $K_3Ag(CN)_4$  has been studied. Unfortunately, however, the experimental equipment did not allow the observation of the resonance region originating from the corresponding isotopic modes in this material. The refractive indices for the laser lines available deter-

mined the "limiting lines" of the  $\omega$ - $k$ -diagram in a way that this sort of experiments was impossible.

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