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EVIDENCE FOR SOFT MODES AT $\vec{q} \neq 0$ IN THE FAR-INFRARED SPECTRUM OF Rb_2ZnBr_4

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The possibility to observe optically inactive and $\vec{q} \neq 0$ soft modes in an indirect way by using far-infrared techniques is investigated. Using the fact that, due to anharmonicity, all modes of lattice vibrations are coupled with each other, the softening of one particular mode can be seen indirectly in the damping of other modes. By applying this idea to the modulated structure Rb_2ZnBr_4, the infrared inactive soft mode at the normal-incommensurable transition, the soft phason mode at the lock-in transition as well as a soft mode behaviour at an intermediate temperature have been observed.

Incommensurable structures have attracted a great deal of interest during the last years[1]. In these systems, below a transition temperature T_i, the atomic positions are shifted periodically, with a characteristic wavevector which is incommensurable with the underlying lattice. In most cases, this modulation becomes commensurable at a temperature $T_c < T_i$. New types of excitations appear in this incommensurable phase, originating from spatial variations of the amplitude or the phase of the modulation wave, called the amplitudon- and phason-modes[2]. The transition to this phase is very often associated with the softening of a lattice mode with a wavevector $\vec{q}_o \neq 0$ situated within the Brillouin-zone. Obviously, this mode is optically inactive, and therefore the softening of this lattice mode will not be seen directly by simple far-infrared techniques. It is expected from theoretical considerations[2], that also one of phason modes should soften at the lock-in transition temperature T_c. Although this mode is in principle optical active, it has not been observed directly due to its small oscillator strength[3].

In this paper we will show that it is possible to study these soft modes at both phase transitions in a rather indirect way. The method is based on the fact that all lattice modes are coupled with each other due to the anharmonicity of the interaction potential. Not the soft mode itself, but the effect of its softening on the other optical active modes is investigated.

The electrodynamic response of a system of damped harmonic oscillators of frequency ω_j and damping constant γ_j is characterized by the frequency dependent dielectric function:

$$\varepsilon(\omega) = \varepsilon(\infty) + \sum_j f_j/\{\omega_j^2 - \omega^2 + i\omega\gamma_j\} \ , \tag{1}$$

where f_j is the oscillator strength of the mode j. The coupling of the modes is reflected in the damping constants γ_j, which are the only entries in Eq. (1) containing information of properties at non-zero wavevectors. Using the usual perturbation theory, these damping constants are given in first order by[4]:

$$\gamma_i = \frac{\pi\hbar}{16N\omega_i} \sum_{k,\ell} \frac{W_{ik\ell}^2}{\omega_k\omega_\ell} [\,(n_k+n_\ell+1)\{\delta(\omega_i-\omega_k-\omega_\ell) -\delta(\omega_i+\omega_k+\omega_\ell)\} + (n_k-n_\ell)\{\delta(\omega_i-\omega_\ell+\omega_k) -\delta(\omega_i-\omega_\ell-\omega_k)\}\,] \ . \tag{2}$$

Here, the summation includes all pairs of modes which fulfil momentum conservation. N is the number of unit cells, the temperature dependent occupation number is given by $n_\ell = [\exp(\hbar\omega_\ell/kT)-1]$ and $W_{ik\ell}$ are the coefficients of the third order term of the anharmonic potential.

If at a $\vec{q}_o \neq 0$ a mode $\omega(\vec{q}_o) = \omega_s$ softens, then one gets for the temperature dependence close to the phase transition

$$\omega_s = \propto |T_t-T|^\beta \ , \tag{3}$$

where β usually equals to a $\frac{1}{2}$[5]. Here T_t is the transition temperature. Near T_t, we have $\hbar\omega_s \ll kT$ and $n_s \gg n_i$ for all $i \neq s$. Therefore, the leading term in Eq. (2) will be $\propto n_s/\omega_s$ which gives in first approximation[6]:

$$\gamma_i(T) \propto T/|T_t-T| \ . \tag{4}$$

The softening of the mode at $\vec{q}_o$ thus results in an increase of the damping constants γ_i of all other modes $i \neq s$ near the phase transition. This can indirectly be observed by measuring γ_i as a function of temperature.

As an example for a normal structural phase transition accompanied by the softening of an infrared inactive mode, in Fig. 1a a part of the far-infrared reflection spectrum of $(CH_3NH_3)_2CuCl_4$ is presented[6]. For the experimentally clearly distinguishable resonances in-

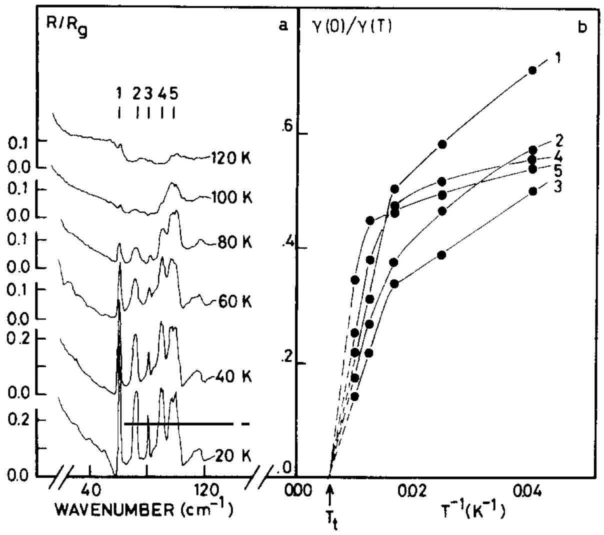

Fig. 1a : Reflectivity R of $(CH_3NH_3)_2CuCl_4$, relative to the reflectivity R_g of a gold sample, as a function of frequency for several temperatures.

1b : Inverse of the normalized damping constant $\gamma(0)/\gamma(T)$ as a function of the inverse temperature T^{-1} for the peaks indicated in Fig. 1a.

dicated by numbers in the figure, the width of the line was taken as a measure for the damping. The damping constants obtained in this way are plotted as a function of the inverse temperature in Fig. 1b. As can be seen from the figure, close to T_t they all show a linear dependence with the inverse temperature, in accordance with Eq. (4).

For systems with high transition temperatures, the sharp lines will coalesque into broad bands, making a direct measurement of γ from the line width impossible. However, it is nevertheless possible to detect a change in γ by carefully measuring the temperature dependence of the transmission of monochromatic far-infrared radiation in this broad band. The relative transmission t^* of electromagnetic radiation through a dielectric slab of thickness d may be approximated, for the case of normal incidence, neglecting multiple reflections and assuming $k \ll n$, by

$$t^* = (1-R)^2 t \ , \tag{5}$$

where $t = \exp(-4\pi d\omega k)$, $R = \frac{(n-1)^2+k^2}{(n+1)^2+k^2}$. Here n and k are the real and imaginary parts of the complex index of refraction $n^* = n-ik = \sqrt{\varepsilon}$. As can be seen from Eq. (5), the dominating term for the transmission is given by k in the exponential leading to t. Therefore we can take n as a temperature independent constant and study the effect of the temperature dependence of $\gamma(T)$ on k only. For frequencies ω close to the low lying resonance frequencies ω_j (i.e. $\omega \approx \omega_i$ and $\omega \ll \omega_j$ for all other $j \neq i$), $k(\omega)$ can be written as

$$k(\omega) = k_i(\omega) + k_o(\omega) \tag{6}$$

$$\text{with} \quad k_i(\omega) = \frac{1}{2n} \frac{f_i \omega \gamma_i}{(\omega_i^2-\omega^2)^2 + \gamma_i^2 \omega^2} \tag{7}$$

$$\text{and} \quad k_o = \frac{1}{2n} \sum_{j \neq i} \frac{f_j \omega \gamma_j}{\omega_j^4} \ . \tag{8}$$

According to Eq. (4), γ_i will increase strongly near the phase transition and the denominator in Eq. (7) will be dominated by $\gamma_i^2\omega^2$, leading to

$$k(T) = \propto |T_t-T|/T + k_o \ . \tag{9}$$

Therefore, k(T) will show a relative minimum at the transition temperature T_t, if k_o is only weakly temperature dependent in this region. As a result, according to

$$t^* \propto t_o(1-4\pi d\omega k_i) = t_o(1-\alpha'|T_t-T|/T) \tag{10}$$

the transmission will show a maximum at T_t. The k_o term has been included in t_o. So by carefully measuring the transmission as a function of temperature at a fixed frequency, possible optical inactive soft modes can be observed indirectly.

We have applied this method to Rb_2ZnBr_4, known to be a modulated structure with T_i = 353 K and T_c = 201 K [7]. As the effect is expected to be rather small, the experimental conditions for measuring the transmission have to be controlled rather accurately. Therefore, a very stable source of monochromatic far-infrared radiation is needed. We used a harmonic generator of microwaves, which is continuously tunable over the range 2 to 25 cm^{-1} [8]. As a detector, a He cooled silicium bolometer was used.

In Fig. 2 the transmission at 7.81 cm^{-1} of Rb_2ZnBr_4 relative to the transmission of the system without sample is plotted against inverse temperature. The figure shows a pronounced maximum at 201 K, and a very small one at 353 K at the two known transition temperatures T_c = 201 K and T_i = 353 K [7]. In addition, at 300 K another well defined maximum is found, indicating an extra phase transition within the incommensurable phase. In Fig. 3 more detailed measurements for temperatures close to T_i are presented, using different frequencies, and all showing the linear T^{-1} dependence of the transmission around T_i, in accordance with Eq. (10).

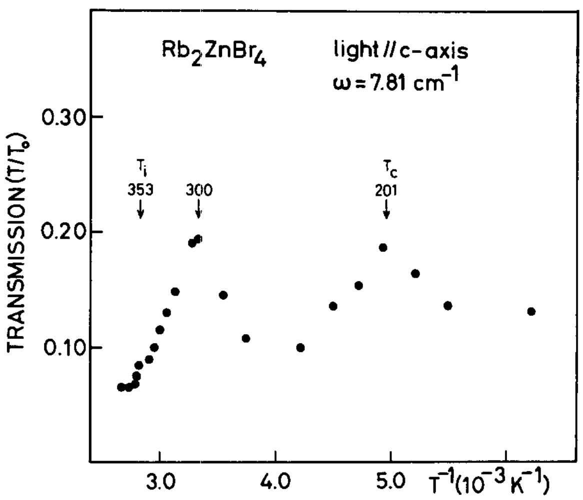

Fig. 2 : Transmission of Rb_2ZnBr_4 at 7.81 cm^{-1} relative to the transmission of the system without sample as a function of the inverse temperature.

These results indicate that one can observe the softening of the modes at both T_c and T_i indirectly, which seemed to be impossible in a direct way[3,9]. As the damping has already increased considerably with temperature around T_i [9], the soft mode contribution is probably relatively smaller here, leading to a smaller effect in the transmission at T_i. As the amplitudon is expected to change only slightly in frequency at the temperature T_c, the $\vec{q}_o$ phason mode should soften at T_c [2]. Therefore, the observed effect at T_c can tentatively be ascribed to this soft $\vec{q}_o$ phason mode. The maximum at

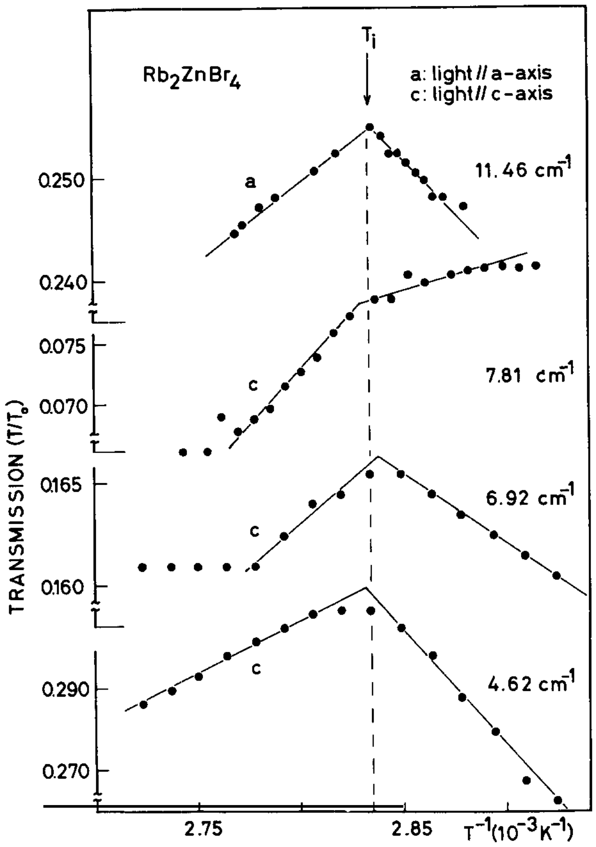

Fig. 3 : Transmission of Rb_2ZnBr_4 relative to the transmission of the system without sample for several frequencies as a function of the inverse temperature as measured close to the normal-incommensurable transition temperature T_i.

300 K indicates a possible other phase transition within the incommensurable phase, a fact that is also suggested recently by other experiments[10]. This could be the forming of a domain like structure, consisting of commensurate microdomains, before the transition to the real commensurate phase at 200 K takes place[11].

In conclusion we have shown the possibility of indirect investigation of $\vec{q} \neq 0$, infrared inactive soft modes through their contribution to the damping of the other optically active lattice modes. The experiment involves the measuring with very high accuracy of the temperature dependence of the transmission, using very stable monochromatic far-infrared radiation. In this way the optically inactive soft mode at the normal-incommensurable transition as well as the soft mode at the lock-in transition at T_c could be seen in Rb_2ZnBr_4. At T_c, the observed effect can be ascribed to a soft phason. This gives new evidence for the existence of these excitations, characteristic for incommensurable structures but rather hard to observe. At 300 K an intermediate transition within the incommensurable phase has been seen, which is probably a transition to a domain-like structure.

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