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Phonon anomalies in Cu halides

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A great number of the observed phonon anomalies in the zinc-blende phase of Cu-halide crystals are explained by means of a dynamical model. It is assumed that a Cu ion populates four equivalent off-center sites of its ideal position. The off-center Cu^+ population is temperature and pressure dependent. With regard to phonons, this system is described as having a two-mode behavior of the optical vibrations at $\vec{k} \approx 0$; one is due to Cu^+ at the ideal positions and the other is due to Cu^+ at the off-center tunneling states. The latter has basically also a T_2 symmetry, but a shorter correlation length. This explains the appearance, width, and polarization properties of the "extra" lines observed in Raman and infrared, as well as their irregular intensity temperature and pressure dependence. Consequently, the polariton dispersion and the resonant Raman data in CuCl can readily be understood. This model also explains the anomalous intensity $\vec{k}$ and T dependence of the inelastic-neutron-scattering in CuCl. The trend in the phonon characteristics, observed in Cu halides and which is an integral part of this model, follows the same course deduced from the intensity temperature dependence of Bragg x-ray and neutron scattering data.

I. INTRODUCTION

A variety of anomalies are known to exist in the phonon spectra of Cu-halide crystals.[1-14] Attempts have been made to explain the observed anomalies, mainly in CuCl,[1-3] but no systematic interpretation is available, nor a model which deals with the trends of these anomalies in the Cu-halide compounds. In this report a model will be presented, which is capable of explaining the unusual phonon spectrum manifested in CuCl and which is also able to explain the irregular phenomena in the CuBr and CuI spectra. A similar approach was used in the past, in order to account for the temperature dependence of Bragg x-ray and neutron scattering intensities in Cu halides,[15-17] which otherwise could not be understood. In the following we shall modify that model and show its validity for a great number of phenomena observed in the phonon spectra of these compounds.

Several properties of these materials are of special interest. CuCl, CuBr, and CuI are the most ionic crystals of zinc-blende structure (in decending order); according to Phillips[18] their ionicities are close to the point where the NaCl or CsCl structures are preferred. The thermal expansion coefficients $\beta(T)$ follow the respective trend of the ionicities of these compounds.[19] CuCl has a relatively large negative β below 100 K,[19,20] CuBr has a negative β only below 50 K,[19] but β of CuI is always positive.[19] All of them show a relatively high degree of anharmonicity.[21-24] They are known to exhibit several crystalline phases when either temperature or pressure is varied.[25] CuCl, CuBr, and CuI become superionic conductors at high temperatures.[26,27] A significant ionic conductivity was measured at lower temperatures ($T < T_c$) as well.[27] The present study is restricted to the properties of Cu halides at $T < T_c$.

At standard temperature and pressure Cu halides are of zinc-blende structure[25] (ZB, T_d^2). The ZB primitive unit cell contains two atoms; thus one TO and one LO $\vec{k} \approx 0$ lines are expected in the first-order Raman spectrum. Experimentally[1-9] two TO-like modes were observed in CuCl at temperatures down to 2 K (β and γ in Fig. 1), but just one LO phonon (δ) has been detected. TO(β) was found to be much broader than TO(γ).[2,3] In CuBr again two polar modes were observed at room temperature[12,13] (see Fig. 2) but the intensity of the lower-frequency one decreases on cooling and disappears at low temperature.[12,13] CuI is the only one of the Cu halides which shows the expected first-order phonon lines at room temperature[13,14]; but at higher temperature (still in the ZB phase) shows similarly an extra phonon mode.[14] The intensity temperature dependence of the "extra" polar mode in CuBr led to the assumption that this line ought to be a second-order difference combination.[3,12,28] For that reason not much attention was paid to the Raman and ir[29] phonon spectra of CuBr, both experimentally and theoretically. The situation is different with regard to CuCl where the TO(β) could not be considered as a second-order line.[4,5] In this case an intensive research has been performed experimentally,[1-9] which was also dealt with theoretically.[1-3]

Along with the appearance of the extra TO-like line in CuCl, a number of additional anomalies were found. The Lyddane-Sachs-Teller (LST) relation is not obeyed considering either TO(β) or TO(γ) as TO of CuCl.[4,5] Moreover, the polariton dispersion measurements[7] could not be fitted when either TO(β) or TO(γ) were taken as TO, and δ

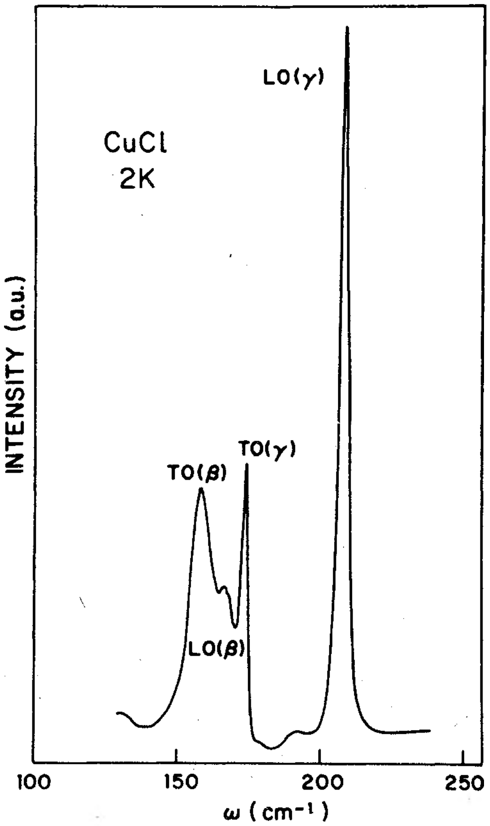

FIG. 1. Raman spectrum of CuCl at 2 K. TO(β), LO(β), TO(γ), and LO(γ) are indicated. (For the assignments see text.)

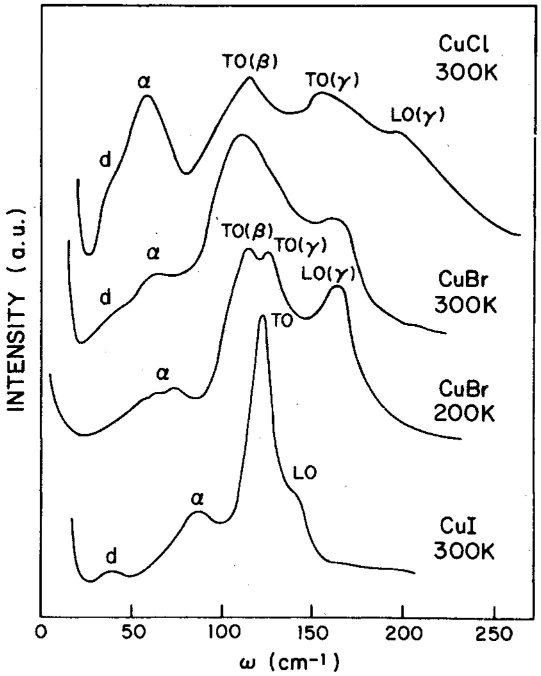

FIG. 2. Room-temperature Raman spectra of CuCl, CuBr, and CuI and that of CuBr at 200 K. In addition to the optical-phonon lines indicated, note the *d* and *α* lines to be discussed in Paper II (Ref. 31).

taken to be the LO frequency. The temperature dependence of TO(β) and TO(γ) intensities does not follow the behavior expected from either a first- or a second-order Raman process.[4,5] While TO(γ) has a halfwidth similar of that of the LO line (δ), TO(β) is much broader.[3] The width of TO(β), TO(γ), and δ is appreciably reduced upon cooling.[3] The whole Raman spectrum looks as if smeared out above 200C. Very recently a drastic reduction of the TO(β) intensity was observed when pressure up to 30 kbars was applied at 77 K.[6]

The room-temperature coherent inelastic neutron scattering spectrum of CuCl consists also of very broad bands and the TO(β) line could not be detected.[28,30] At 4.2 K, TO(β) was only recently observed by neutron scattering.[10,28] At this temperature its intensity seems to be even larger than that of the TO(γ) line at $\vec{k} \approx 0$. For increasing $|\vec{k}|$ in the [111] direction, the TO(β) line intensity gradually decreases and for $|\vec{k}|$ approaching about half of the Brillouin zone it smears out as seen in Fig. 3. A smearing of the LA branch at large $|\vec{k}|$ in the [110] direction was also observed very recently by neutron scattering at temperatures above 150 K.[11]

A theoretical explanation is needed for all the β-γ phonon anomalies in CuCl described above as well as their temperature and pressure dependence. Any model for CuCl should account also for the similar anomalies observed in CuBr and CuI. The theoretical model of Krauzman *et al.*[2] is successful in reproducing the shape of the β-γ Raman spectrum of CuCl at 40 K. This model assumes a third-order anharmonic interaction between the TO and a background of a two-phonon continuum having a singularity at a frequency close to that of the TO. This interaction results in repelling the TO(γ) and giving rise to the additional TO(β) line. The fit of the Raman spectrum in the β-γ region was done at 40 K using five parameters.[1] A similar model was presented by Fukumoto *et al.*[3] and was fitted to Raman spectra at different temperatures. The main disagreement between the two models is in the frequency of the singularity; while it is 170 cm⁻¹ in the first model it is assumed to be at 146 cm⁻¹ in the second one. Shand *et al.*[1] were also successful in predicting the pressure dependence of the β-γ lines of CuCl at 77 K.[6]

By now only the anomalies of optical phonon spectra were mentioned. Naturally no information is expected from first-order Raman and infrared

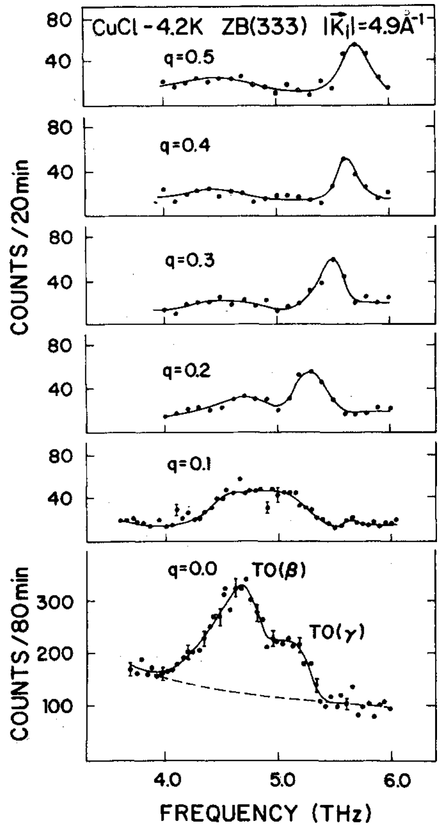

FIG. 3. Inelastic neutron scattering of CuCl in the TO geometry at 4.2 K (full circles), by various $|\vec{k}|$ values in the [111] direction. The lines are drawn to guide the eye. The data are from Dorner *et al.* (Ref. 10). Receiving it prior to publication is highly appreciated.

spectra about acoustical phonons. Nevertheless, a weak TA line (marked *d* in Fig. 2) was detected in a polarized Raman spectrum of CuCl, when the rest of the spectrum did not interfere with that line.[28] A similar TA line was observed in CuBr and CuI as well.[13,28] The following paper[31] deals with the disorder-induced TA line in the mixed-crystal systems $CuCl_xBr_{1-x}$ and $CuBr_xI_{1-x}$. In these cases the TA phonon line is extraordinarily enhanced in the Raman spectra.

At elevated temperatures (> 100 °C) a very intense low-frequency scattering is observed,[31] which is characteristic of superionic conductors. The low-frequency scattering dominates the Raman spectrum and the optical phonon lines smear out.[14,31] This will be further explained in the following paper.[31]

The phonon anomalies are not the only irregularities found in these compounds. X-ray and neutron diffraction were studied in the *ZB* phase of cuprous halides by Hoshino and co-workers.[15-17] They observed an anomalous variation of the Bragg reflected intensity with temperature which started to be significant at ~ 370 K in CuI,[16] at ~ 150 K in CuBr,[17] and presumably at low temperature in CuCl.[15] It was suggested that while the Debye factor of the anions decreases with increasing temperature in a normal way, the Debye factor of the Cu^+ ions increases with temperature. This was found to be consistent with two models which explain the data equally well.[15] In the first one, the disorder model, it is assumed that copper may occupy one out of four equivalent off-center sites located on the [111] directions towards the four faces of the tetrahedron formed by the anions (see Fig. 4). The second one, the anharmonic anisotropic model, allows for copper to occupy a volume of "tetrahedral symmetry" around its ideal position (Fig. 4). The conceptual difference between them is mainly in the shape of the potential wells and the ratio between the dwelling time and the flight time. Which of these models gives a better physical description, may depend on the temperature.

We shall modify the first model[15] and show that it may account for the various phonon irregularities as well as those of Bragg x-ray and neutron scattering intensities.

In Sec. II the model and its physical origin and meaning are presented. In Sec. III, the experimental data is discussed in terms of this model. A summary is given in Sec. IV.

II. MODEL

Generally speaking we adopt the overall scheme of the disorder model[15] (model 1) used for the interpretation of the unusual intensity temperature dependence of Bragg x-ray and neutron scattering. It is known that Cu halides show high anharmonicity. We propose that their anharmonicity is so high as to generate secondary off-center minima in the cation potential energy. These four off-center minima are located at a distance r_0 in the [111] direction, away from each one of the four anions by which the Cu^+ is surrounded (see Fig. 4).

What might cause the appearance of these additional energy minima in the potential energy of Cu^+? It is difficult to give a formal answer to this fundamental question. However, there exist a number of facts from which an explanation can be deduced. The 3*d* and 4*s* electronic shells in Cu are very close in energy[32] and therefore an increase in the admixture of these electrons in the bonding may occur when Cu approaches three of its nearest-neighbor anions. This may result in an additonal covalent attractive potential $\Phi_{att}(r)$ between Cu and the halogens, which to first order competes with

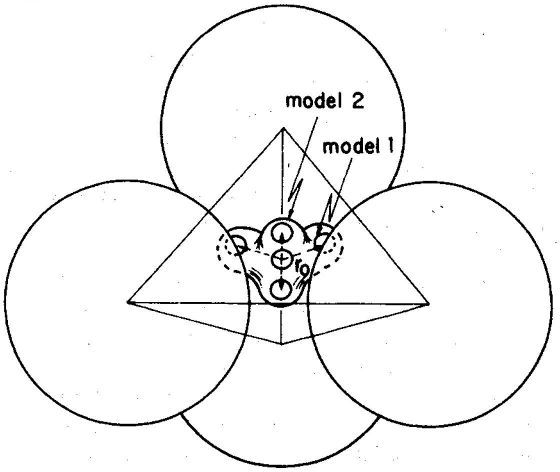

FIG. 4. The two proposed models: the small circles represent the five possible Cu^+ sites in model 1, the "volume" encircling these sites represents the possible Cu^+ location in model 2. r_0 is indicated (see text).

the enhancement of the usual repulsive potential $\Phi_{rep}(r)$ generating an off-center minimum r_0 away from the center.

The electrostatic potential $\Phi_{coul}(r)$ and the polarization potential $\Phi_{pol}(r)$ are also usually used to compute off-center potential minima.[33] These may reduce the overall potential energy $E(r)$ when Cu^+ is a distance r away from the center, but are second-order approximations due to their relatively low r dependence.

The strength of $\Phi_{att}(r)$ depends on the electronegativity of the halide ions; the larger the electronegativity the bigger will be the share of the $3d$ electrons in the bonding.[32] This is consistent with the trend found in Cu halides in regard with the participation of the $3d$ electrons in the bonding.[34] Cu appears with either a single or a double valency in these compounds[35]: CuI_2 is unstable relative to CuI and while CuBr, $CuBr_2$, CuCl, and $CuCl_2$ exist, CuF does not and only CuF_2 exists.

On the other hand, the degree to which Cu^+ can move from its ideal site, depends on the difference between the nearest-neighbor distance R_0 and the sum of the hard-sphere radii $R(Cu^+)$ and $R(X^-)$ of copper and halogen ions, respectively: $d = R_0 - [R(Cu^+) + R(X^-)]$, when d is small, $\Phi_{rep}(r)$ is high. It is known that d grows going from CuI to CuCl.[24] The trends of the electronegativity and that of d in the various Cu halides may allow a deep off-center well minima in CuCl, less in CuBr and least in CuI. This follows the trend found in the temperature dependence of the anomalous Bragg x-ray and neutron diffraction intensities: the anomaly starts to be appreciable in CuI,[16] at about 370 K, when the lattice parameter may permit sufficiently deep off-center minima, at about 150 K in CuBr,[17,36] and it seems to be significant even at very low temperature in CuCl.[11,15]

In a number of copper-doped materials, Cu^+ was found to occupy off-center sites.[37] Moreover, CuCl, CuBr, and CuI become superionic conductors at around 450 °C,[27] and the fact that Cu ions occupy off-center sites in these cases is well established.[26] This hints that there should be a mechanism that permits the Cu ion to change its environment. namely, to approach three of its first-neighbor anions, departing from the fourth one.

A variety of experiments show that Cu $3d$ electrons participate in the bonding. It is concluded[34] that $3d$ are the highest bands in Cu-halide valence bands, where an admixture of p-d electrons occurs. This p-d hybridization increases from CuI to CuCl.[34] The p-d hybridization being dynamical under the influence of phonons also explains the temperature broadening of photoemission from these compounds.[38] This picture is in line with the negative sign of the electro-optic coefficient in CuCl contrary to most of the *ZB* crystals.[4]

We introduce two modifications to the disorder model[15] (model 1). (a) A cation may occupy its ideal position *as well as* the four equivalent off-center sites. The relative population of central and off-center sites depends only on the potential energy difference Δ of the respective wells minima. To first approximation Δ is a function of temperature and pressure via the lattice constant $a(T,P)$. A contraction of the lattice increases the repulsive potential and therefore increases Δ. This is known in the case of off-center impurity as Li^+ in KCl.[39] This may explain the existence of off-center sites in CuCl at very low temperature; the lattice parameter $a(T)$ of CuCl increases below 100 K and $a(0\ K) \approx a(200\ K)$.[19,20] This fact should reduce Δ in CuCl maintaining finite off-center population down to very low temperature! (b) We assume a *dynamical* model in which the cation may tunnel among all five wells; the tunneling probability being much larger among the four equivalent off-center wells. This means that the lifetime of the cation in the central well is much longer than that of the cation in an off-center well. It should be emphasized that analysis of the T dependence of Bragg x-ray and neutron scattering intensities in Cu halides is not sensitive to a possible internal motion of Cu^+ among the different sites. But in *ZB* phase of Cu halides, though at high temperatures, the NMR signal narrows due to a rapid motion of Cu^+ ions.[27,40] Moreover, a substantial fraction of Cu^+ ions was assumed to occupy ⟨111⟩ interstitial sites[40] and the motion of Cu^+ corresponds to jumps among the regular and the interstitial sites. The ionic radius of Cu^+ is small, giving rise to its high diffusion constant. The anions on the other hand do occupy their ideal positions.

A second potential well minimum cannot be treated by usual anharmonicity. What does such a model imply in terms of lattice vibrations? In addition to the phonon produced by the regular site cations, more vibrations will be generated due to the off-center cations ("off-center vibrations"). It may be analogous to the case of mixed crystals in the sense that the force constants between the halogen ions and the central or off-center Cu^+ are different. Using the vocabulary of mixed crystals, it is assumed that this system may be described as having a two-mode behavior in the optical phonons and a one-mode behavior in the acoustical phonons. This may be more meaningful for the optical phonons at small $\vec{k}$, for which the vibrations of the tetrahedra containing off-center copper are in phase and therefore they are not too much affected by the degree of correlation between off-center copper. For higher $|\vec{k}|$ values one has to deal with a dynamical disorder.

It is now required to show that in spite of the dynamical disorder introduced, it is still possible to deal with phonons in such a crystal (see Sec. II A), and that the assumption of tunneling may preserve the T_d symmetry of the off-center vibrations at small $|\vec{k}|$ (see Sec. II B).

A. Phonons in semiordered crystals

In dealing with the phonon concept under the assumption of the present model we shall follow Shuker and Gammon for phonons in amorphous materials.[41] We shall refer to neutron scattering by phonons in order to cover the whole range of the phonon dispersion curves. When referred to Raman scattering the density fluctuations should be replaced by the dielectric constant fluctuations.[41]

Following Van Hove,[42] the coherent-scattering cross section for slow neutrons is proportional to the Fourier transform of the space-time correlation function of the fluctuations in the density of the material. The correlation function can be written as

$$G(\vec{r},t)=(1/\rho)\langle\Delta\rho(\vec{r}',t')\Delta^*\rho(\vec{r}'+\vec{r},t'+t)\rangle\,,$$

where the self-correlation is omitted. The correlation is between fluctuations in the density at time $t+t'$ and point $\vec{r}+\vec{r}'$ with those of time t' and point $\vec{r}'$. The angular brackets are for thermal average. The density can be expanded in terms of normal coordinates $Q_j(t)$. The correlation function, to the first-order neutron scattering becomes

$$G(\vec{r},t)=\left\langle \sum_{j,j'} \frac{\partial\rho(\vec{r}')}{\partial Q_{j'}} Q_{j'}(t') \frac{\partial^*\rho(\vec{r}'+\vec{r})}{\partial Q_j} \times Q_j^*(t+t')\right\rangle\,, \tag{1}$$

where the time dependence appears only in the normal coordinates. Separating spatial and temporal parts and dropping the summation on j', because of the orthogonality and the statistical independence of the normal coordinates, one obtains

$$G(\vec{r},t)=\sum_j \left\langle \frac{\partial\rho(\vec{r}'+\vec{r})}{\partial Q_j} \frac{\partial\rho^*(\vec{r}')}{\partial Q_j}\right\rangle \times \langle Q_j(t')Q_j^*(t'+t)\rangle\,. \tag{2}$$

The time-correlation function yields the frequency dependence of the intensities, while the spatial correlation functions of the density fluctuations

$$R(\vec{r},Q_j)=\left\langle \frac{\partial\rho(\vec{r}+\vec{r}')}{\partial Q_j} \frac{\partial\rho^*(\vec{r}')}{\partial Q_j}\right\rangle$$

essentially reflect the spatial correlations of the atomic displacements. This means that the correlation range of $R(\vec{r},Q_j)$ will be that of the mode Q_j. In perfect crystals the translational symmetry yields a long-range correlation and the phonons are represented by plane waves $\exp(i\vec{k}\cdot\vec{r})$ throughout the medium. In this case the spatial correlation function should also be periodic. The Fourier transform of the correlation functions is then $A(\vec{k}_j)[\delta(\vec{k}_j-\vec{q})]$, $\vec{k}_j$ is the wave vector of the mode j and $\vec{q}=\vec{k}_s-\vec{k}_i-\vec{G}$ is the momentum transfer. This leads to the usual momentum conservation rule.

In disordered systems the phonon representation is no longer an exact plane wave. One should then introduce a decay parameter $\Lambda_j(\vec{k}_j)$ which reflects the correlation length of the mode Q_j.[41] $\Lambda_j(\vec{k}_j)$ depends on the extent of the disorder as well as the wavelength and the propagation direction of the phonons. When the spatial exponential decay is introduced, the spatial-correlation function also decays exponentially:

$$R(\vec{r},Q_j)=A(Q_j)\exp(i\vec{k}_j\cdot\vec{r})\exp[-|\vec{r}|/\Lambda(\vec{k}_j)].$$

The Fourier transform of this function is proportional to $\Lambda_j^3/[1+(\vec{q}-\vec{k}_j)^2\Lambda_j^2]^2$.

In this result all the information is contained: (a) the scattered intensities will be proportional to Λ_j^3—the "volume of the mode" for $\vec{q}\approx\vec{k}_j$ and the intensity drops as the phonon-correlation length decreases. (b) As Λ_j decreases, the condition of momentum conservation relaxes, so that modes with wavevectors $\vec{k}\neq\vec{q}$ will contribute to the scattered intensities, being centered at ω where $g(\omega)$, the phonon density of states, is large enough. Therefore phonons at the Brillouin zone boundaries contribute most. A long-wavelength mode of oscillation is only slightly affected by the disorder so that its correlation length is large. This is nicely demonstrated by the appearance of cooperative vibrational modes in liquids for small $|\vec{k}|$.[43] A long wavelength averages over the disordered ions; the number of "proper" ions is sufficient to produce a phonon. For larger $|\vec{k}|$ the correlation length decreases and so does the intensity. Moreover, the $\vec{k}$ selection rule relaxation causes smearing of the phonon lines. This is a known phenomenon in disordered materials. Such a $|\vec{k}|$ dependence reduction in the intensities of neutrons scattered inelasticly from magnons was observed[44] in mixed $Rb_2Mn_{0.5}Ni_{0.5}F_4$ when compared with scattering from magnons of pure K_2MnF_4. In the mixed crystal a reduction of an order of magnitude is obtained going from $\vec{k}\approx 0$ to $\vec{k}=\vec{k}_{max}$. Another example[45] is that of neutron scattering from phonons in the tetragonal phase of $NH_4Cl_{0.46}Br_{0.54}$ at 96.5 K. For larger $\vec{k}$ in the [100] direction, the neutron scattering peak height decreases and smears out. No information is given there for any direction different from [100]. It is not only the magnitude of $|\vec{k}|$ that affects the phonon intensities but also its direction. In a direction where the density of ions is larger, the correlation length will be smaller. The data of the intensity decrease of the neutron scattering from magnons is shown in the [100] direction[44] for which this effect should be the largest. In zinc-blende materials this has to occur in the [110] direction for which the packing is the most dense and the correlation length therefore is expected to be the shortest.

B. Vibrations' symmetry at $\vec{k} \approx 0$

The model potential for the off-center tunneling Cu^+ is an appropriate three-dimensional analog of the one-dimensional double-well harmonic oscillator. We assume four potential minima A, B, C, D each displaced r_0 from the center of the tetrahedron formed by the anions (see Fig. 4), where the joining vectors are

$$\vec{r}_0(A)=\tfrac{1}{4}(-\delta,-\delta,-\delta)a,\ \vec{r}_0(B)=\tfrac{1}{4}(-\delta,\delta,\delta)a,$$

$$\vec{r}_0(C)=\tfrac{1}{4}(\delta,-\delta,\delta)a,\quad \vec{r}_0(D)=\tfrac{1}{4}(\delta,\delta,-\delta)a;$$

$r_0=\frac{1}{4}\delta a\sqrt{3}$ and a is the lattice constant.

For simplicity, each displaced harmonic oscillator potential is characterized by only one frequency (i.e., is isotropic). Our result remains unaltered also for an anisotropic potential well. This means that the potential wells are of the form $V_A=\frac{1}{2}m\omega_0^2[\vec{r}-\vec{r}_0(A)]^2$ for the case in which the Cu^+ occupies the A site. The fifth deep central potential well is not included in the present treatment, because of the lower tunneling rate between it and the four equivalent off-center positions. The final result remains unaltered when the fifth well is included, because of the isotropic behavior of its harmonic oscillator function under the point-group symmetry operations belonging to T_d.

For $\vec{k}\approx 0$, when the vibrations of each tetrahedron are considered to be in phase and therefore can be studied separately, one can follow the usual procedure of impurity tunneling states (for example, Li^+ in KCl), as treated by Gomez *et al.*[46] The energy levels of the lowest-lying multiplet are found from the correct linear combinations of the basis vibrational states. For these ground-state splittings, the basis states are normalized simple-harmonic-oscillator (SHO) ground-state wave functions, centered at each well minimum, labeled $|a\rangle$, $|b\rangle$, $|c\rangle$, and $|d\rangle$.

$$|a\rangle=\left(\frac{m\omega_0}{h}\right)^{3/4}\exp\left[-\left(\frac{m\omega_0}{2h}\right)[\vec{r}-\vec{r}_0(A)]^2\right]. \quad (3)$$

The correct linear combination of the basis states are determined by a group theoretical method: one can compute the character of each point-group symmetry operation belonging to T_d in the field of the four ground-state functions $|a\rangle|b\rangle|c\rangle|d\rangle$. Then one can look for the irreducible representations of T_d, which are contained in the reducible representation of T_d symmetry spanned by the four functions. There are only two such irreducible representations: three fold degenerate T_2, which is Raman and ir active, and A_1, which is Raman but not ir active. These are the only possibilities of the vibrating tunneling off-center Cu^+. If the off-center positions were isolated, we should get indeed the two possibilities with energies $E(A_1)$ and $E(T_2)$ where

$$E(A_1)=(E_0+3\beta)/(1+3S)$$

and

$$E(T_2)=(E_0-\beta)/(1-S),$$

where

$$\beta=\langle a|H|b\rangle=\langle b|H|c\rangle\cdots \text{etc.};$$

$$S=\langle a|b\rangle=\langle b|c\rangle\cdots \text{etc.}; E_0=\hbar\omega_0;$$

analogous to an impurity state. But the off-center Cu^+ is not isolated and there exists a certain correlation length of the phonon in which it participates. It is assumed that each off-center Cu^+ tunnels among *four sites* and the correlation length of the off-center phonon is therefore shorter than that of the central phonon. The Cu^+ tunneling between central and off-center sites is of much lower rate than that among the off-center sites and can be ignored in here. The relative smaller correlation length of the off-center phonons affects the width of this phonon line as well as its "purity" (conservation of $\vec{k}$). The shorter the correlation length, the lesser the polarization selection rules will be obeyed. This should be noticed in polarized

Raman spectra and in infrared absorption and reflection spectra, mainly for the off-center phonons. At small enough $|\vec{k}|$ where the off-center phonon correlation length is not too short, the selection rules relaxation may be treated as a perturbation. Therefore we continue with the assumption that the correlation length is sufficiently long. Under this assumption the system is considered to have a *two-mode* behavior and one can thus deal with the off-center case separately; this is justified at $\vec{k}\approx 0$, where the vibrations of the tetrahedra are in phase and therefore every tetrahedron can be treated individually.

The off-center Cu^+ occupies a *tunneling state* in each off-center Cu^+ cell and the unit cell responsible for the off-center vibrations can be considered as containing two atoms. From group theory at $\vec{k}=0$ only three degenerate optical vibrations are expected. This means that from the two vibrational possibilities A_1 and T_2, only the threefold degenerate T_2 can exist. This mode is Raman and infrared active and splits into an LO and TO mode. Therefore no information about the splitting energy $E(A_1)-E(T_2)$ can be gained. This situation is different from the case of an off-center impurity such as Li^+ in KCl.[46] In that case no definite off-center impurity unit cell can be asserted, thus all the off-center impurity vibrational possibilities can exist. The selection rules for the off-center Cu^+ vibrations at $\vec{k}=0$ are then the same as in the ideal case with T_2 symmetry. On the other hand, if a static model were assumed, an off-center vibration would have a lower symmetry. In that case splittings as well as different polarization selection rules should have been observed.

Under the conditions stated above, it might be possible to approach the problem of lattice dynamics of the off-center phonons using the combination of the following four dynamical matrices. Assuming Cu^+ are all in A positions (one of the four possibilities A, B, C, D mentioned), a 6×6 dynamical matrix $\underline{D}^A(\vec{k})$ based on the Born–von Kármán theory, is obtained.[47] $\underline{D}^A(\vec{k})$ is calculated taking into account the different distances and force constants between the off-center Cu^+ and the anion sublattice. This is reflected in the Coulombic matrix $\underline{C}(\vec{k})$, as well as in the repulsive matrix $\underline{R}(\vec{k})$. The same procedure is repeated for the off-center Cu^+ being all in B, C, or D sites, to obtain the dynamical matrices $\underline{D}^B$, $\underline{D}^C$, $\underline{D}^D$, respectively. Since off-center Cu^+ is in a tunneling state, where the off-center positions are all equivalent, one can take an average dynamical matrix $\underline{D}(\vec{k})$:

$$\underline{D}(\vec{k})=\tfrac{1}{4}[\underline{D}^A(\vec{k})+\underline{D}^B(\vec{k})+\underline{D}^C(\vec{k})+\underline{D}^D(\vec{k})]. \qquad (4)$$

This dynamical matrix was calculated and was found to have exactly the same symmetry as that of the normal *ZB* structure dynamical matrix. Therefore the phonon branches, which are the solutions of the usual secular equation $|\underline{D}-\underline{M}\,\underline{I}|=0$ will exhibit again the same symmetry as the normal *ZB* phonons. This procedure is valid only as long as the phonon concept is still good—as long as the correlation length is long enough (near $\vec{k}=0$). The fact that the off-center Cu^+ are not all at the same site (A, B, etc.) as assumed for obtaining D^A, D^B, etc. is a second-order approximation to the off-center frequency. This will be reflected only in the second-nearest-neighbor Cu^+-Cu^+ interaction, which has smaller contribution to the energy and thus to the frequency.[47] Nevertheless, this is responsible for an additional width of the off-center frequency relative to the width of the normal phonon branches.

Using the above method, an attempt was made to calculate the off-center phonon frequencies at $\vec{k}\approx 0$ in CuCl. We started from a rigid ion model well fitted to the normal dispersion curves $\omega_j(\vec{k})$ in CuCl measured at 4.2 K by Prevot *et al.*[11] In order to obtain a decrease in the off-center TO and LO frequencies as function of the off-center distance r, an addition of steep attractive potential was needed. This attractive potential, as explained previously, is necessary for the formation of the secondary off-center minima.

We have used the "disorder model"[15] together with assumption of the fifth central well and the tunneling among the wells. The "anharmonic model"[15] is equivalent to the disorder model as far as x-ray and neutron scattering are concerned as long as the distance of the off-center sites from the central one is not too big, relatively to the nearest-neighbor distance.[15] The phonon spectra may be used for comparing the two models. The anharmonic model requires barrier heights of the order of kT or less and flight time that is long compared to dwelling time. This is expected to show up in the phonon spectrum as a very broad and smeared line of the optical phonon region. This may be the case at sufficiently high temperature. It is certainly not the case in CuCl below room temperature.

III. DISCUSSION

We shall now discuss the available experimental data in view of the proposed model. The main part of the discussion is devoted to CuCl which was investigated much more intensively then the other Cu halides. In the case of CuCl, the neutron scattering data at low temperature[10] are very illuminative, therefore $\vec{k}\approx 0$ and $|\vec{k}|>0$ will be dealt with separately.

A. CuCl, $\vec{k} \approx 0$ phonons

The measurements of Bragg x-ray intensity were not extended below room temperature, but it can be inferred from the experimental data[15] that the anomalous intensity temperature dependence starts at lower temperature. Calculating the increase of $\langle u^2 \rangle$ of Cu$^+$ from the neutron scattering data, Prevot *et al.*[11] showed that the unusual behavior starts at low temperature. Assuming that the Cu$^+$ potential has a central and off-center minima, two sets of phonons are expected: these in which the central Cu$^+$ is involved (γ) and these in which the off-center Cu$^+$ is involved (β); both exhibit the same symmetry.

The Raman spectrum does contain two TO lines: $\omega[\mathrm{TO}(\beta)] = 149$ cm^{-1} and $\omega[\mathrm{TO}(\gamma)] = 173$ cm^{-1} (at 77 K).[3,28] TO(β) is much broader than TO(γ) and has the same polarization configuration.[2] Another first-order line at 210 cm^{-1} (δ) has the polarization of an LO,[2] and a width of the order of TO(γ),[3] and is thus the corresponding LO(γ). But an extra low-intensity line appears,[1] also of LO polarization,[2] at 162 cm^{-1}.[5,6,28] This line could not be interpreted by previous models.[1] We assign this line to be LO(β) (see Fig. 1). These four line frequencies should also be obtained from the analysis of the infrared spectrum. In both ir reflection and absorption a double oscillator spectrum is obtained.[8] From Kramer-Kronig analysis the LO(β) frequency comes out to be ~161 cm^{-1},[4] which is in good agreement with that of the Raman frequency, taking into account its expected width and the fact that it is placed between TO(β) and TO(γ), both of much higher intensity than LO(β).

A different way to examine this line would be via resonance Raman effect. From the work of Oka *et al.*,[9] no conclusion can be reached on this matter although they show that TO(β) and TO(γ) merge into one broad line. An explanation for this may be found in resonance enhancement of the LO(β) that lies in between. Preliminary experimental reexamination of the resonance work at our laboratory confirms this fact, but shows also Raman lines at frequencies around 2LO(β) and LO(β) + LO(γ) as well as at 2LO(γ).

The LST relation is not properly obeyed when either TO(β) or TO(γ) are considered together with LO(γ).[4,5] β and γ are polar modes and therefore contribute to the dielectric response. Without damping the dielectric function is then written as

$$\epsilon(\omega) = \epsilon(\infty) + S_\beta \omega_\beta^2/(\omega_\beta^2 - \omega^2) + S_\gamma \omega_\gamma^2/(\omega_\gamma^2 - \omega^2),$$

where S_β and S_γ are the oscillator strengths of β and γ, respectively. Consequently[48] the LST relation is

$$\frac{\epsilon_0}{\epsilon_\infty} = \left(\frac{\omega[\mathrm{LO}(\beta)]\omega[\mathrm{LO}(\gamma)]}{\omega[\mathrm{TO}(\beta)]\omega[\mathrm{TO}(\gamma)]}\right)^2 .$$

With the values $\omega[\mathrm{TO}(\beta)] = 149$ cm^{-1}, $\omega[\mathrm{LO}(\beta)] = 161$ cm^{-1}, $\omega[\mathrm{TO}(\gamma)] = 173$ cm^{-1}, $\omega[\mathrm{LO}(\gamma)] = 210$ cm^{-1} and $\epsilon_\infty = 3.61$ at 77 K, one obtains $\epsilon_0 = 6.21$ compared with $\epsilon_0 = 6.1$ as measured directly by Potts *et al.*[5] at the same temperature.

The polariton dispersion is[49]

$$c^2 q^2/\omega^2 = \epsilon(\omega), \tag{5}$$

where $\epsilon(\omega)$ contains contributions from the β and γ modes. In order to derive the polariton dispersion, the individual strength functions are required. These are usually derived from infrared data, but the contradictory infrared results[8,29,50] led us to use a different procedure for the evaluation of S_β and S_γ.

The ratio S_β/S_γ can be obtained from the ratio of the reduced Raman intensities $[I/(n+1)]$ of TO(β) and TO(γ), assuming that the Raman matrix element does not vary much with frequency.[51] This seems reasonable due to the small frequency separation of these two modes. The great similarity between the Raman spectrum (see Fig. 1) and the ir absorption spectrum of Ikezawa at 2 K (Ref. 50) further justifies our assumption. In order to obtain S_β and S_γ individually the second relation used is $\epsilon(\omega[\mathrm{LO}(\gamma)]) = 0$. The frequency of LO($\gamma$) is far from the β-γ region and the absorption coefficient reaches zero at LO(γ) frequency, unlike the case of LO(β).[50] Using this procedure we obtain $S_\beta = 1.67$ and $S_\gamma = 0.90$ which yield $\epsilon_0 = \epsilon_\infty + S_\beta + S_\gamma = 6.18$. This value agrees well with the measured $\epsilon_0 = 6.1$.[5] From these values the second zero of the dielectric response yields LO(β) = 161 cm^{-1} compared with LO(β) = 162 cm^{-1} obtained from the Raman spectra at 77 K.[5,6,28]

Shand *et al.*[7] carried out polariton dispersion measurements, but could not fit their data to a curve calculated assuming one oscillator either TO(β) or TO(γ) along with LO(γ).[7] Figure 5 shows the good agreement between the experimental data of Ref. 7 and the dispersion curve calculated from Eq. (5). Introducing damping will even improve the fit.

A very recent report on CuCl polaritons[52] provides more data points, which are also indicated in Fig. 5. These points are at higher $\vec{k}$ values and reassure that the lower polariton curve stems from the β mode. Moreover, the fact that the γ polariton dispersion could also be measured is of special importance for the present work, for it is in agreement with our basic assertion of two oscillators and is consistent with the calculated strength functions.

We assumed that the correlation length of the β phonon is shorter than that of the γ phonons. In TO scattering geometry $x(zx)z$, LO(γ) is completely supressed (at low temperatures), which means that the LO(γ) polarization selection rules are

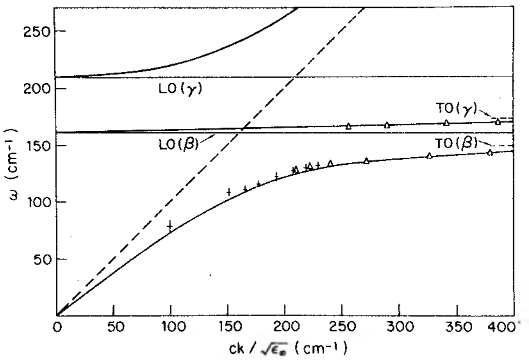

FIG. 5. Polariton dispersion in CuCl at 77 K. Crosses and triangles are data points of Refs. 7 and 52, respectively. The curves were calculated using Eq. (5) with two oscillators: $\omega_\beta = 149$ cm^{-1}, $S_\beta = 1.67$, $\omega_\gamma = 173$ cm^{-1}, $S_\gamma = 0.90$ (see text).

properly obeyed.[2,28] On the other hand, in the pure LO geometry $z(xy)\bar{z}$, a significant intensity at 140–170 cm^{-1} is detected,[2,7] in spite of the measures taken to prevent reflections from the back surface.[7] The shape of this spectral structure differs from the TO(β)-TO(γ) one found in TO geometry: the gap between TO(β) and TO(γ) is filled by the allowed LO(β) and the TO(γ) intensity is greatly supressed.[2,7] The shorter correlation length of β phonons perturbs the polarization selection rules, causing the appearance of TO(β) in this forbidden configuration. In mixed crystals ($\mathrm{GaP}_x\mathrm{As}_{1-x}$),[53] having a two-mode behavior, selection rules are not properly obeyed for the line corresponding to the smaller concentration end and thus have a shorter correlation length. The reminiscence of the TO(γ) line may be due to an interaction with TO(β). On the other hand in the $z(xx)\bar{z}$ geometry, where both TO and LO are forbidden, no scattering is detected.[7] The lack of scattered intensity in this geometry also rules out the assumption of a possible second-order process.[2]

The same arguments may hold for the hump at the LO(β) frequency, observed in the infrared reflection[29] and absorption[50] spectra. The relaxation of $\vec{k}$ selection rule for the β phonons causes contribution from $\vec{k}$ different from $\vec{k}_0$ and their LO modes may couple directly to the photons, even at small angle. A nonzero angle is known to induce a weak LO line in the infrared measurements.[54] A weak LO line was observed even at zero angle in infrared absorption of thin $\mathrm{CdS}_x\mathrm{Se}_{1-x}$ films,[55] where the phonon correlation length is sufficiently short.

Raman, resonance Raman, infrared, and polariton spectra as well as the LST relation suggest that the observed line between TO(β) and TO(γ) is LO(β). There is still the question of its intensity. At least at low temperatures it is evident that the intensity of LO(γ) exceeds that of TO(γ), while the opposite is true for LO(β) and TO(β) (see Fig. 1). According to the present model β stands for optical phonons involving off-center Cu$^+$ sites. In this case there is an important role of the 3*d* electron that makes the bonding more covalent. In the Cu halides the ionicity decreases in the order CuCl, CuBr, CuI,[18] and the ratio $I_{\mathrm{LO}}/T_{\mathrm{TO}}$ decreases in the same order.[9] This is consistent with the observation that $I_{\mathrm{LO}(\beta)}/I_{\mathrm{TO}(\beta)}$ is smaller than $I_{\mathrm{LO}(\gamma)}/I_{\mathrm{TO}(\gamma)}$.

The relative population of central and off-center Cu$^+$ depends on the potential energy difference Δ of the respective well minima. The lattice parameter, which is temperature and pressure dependent, is one of the factors that determine Δ. Whenever this factor is dominant, it is possible to qualitatively explain the temperature and pressure dependence of the relative population of central and off-center Cu$^+$. On the other hand, the Raman relative intensities do not directly reflect the relative-center–off-center Cu$^+$ populations because of the different oscillator strength and the changes in the phonon correlation length. For these reasons any qualitative explanation of the temperature and pressure dependence of the ratio $I_r = I_{\mathrm{TO}(\beta)}/I_{\mathrm{TO}(\gamma)}$ is due to be oversimplified. Nevertheless, when the intensities of TO(β) and TO(γ) are compared at different temperatures, the minimum of off-center Cu$^+$ population comes out to be around the temperature of the minimal lattice constant, namely, around 90 K.[19] Neither TO(β) nor TO(γ) follows the Bose $\bar{n}+1$ behavior, though the combined area under these peaks shows approximately such a behavior.[4] This was checked for the 40–120-K range using the impressive polarized spectra of Prevot.[28] According to his data, on going from 40 to 120 K the intensity of TO(γ) grows faster then $\bar{n}+1$ and the intensity of TO(β) slower than $\bar{n}+1$. From our data at higher temperature (110- to 540 K) the opposite seems to occur, namely, TO(β) exceeds the $\bar{n}+1$ behavior while TO(γ) deceeds it.[31] The same conclusions can be drawn from the Raman data of Potts *et al.*[5] and that of Kaminow and Turner.[4]

It should be mentioned that for $kT < \Delta$ (Δ being the energy difference between central and off-center well minima) the relative population should vary exponentially, but this is not the case for $\Delta \sim kT$. Δ is temperature dependent as discussed above. As far as one can judge from the Raman intensities in CuCl it seems that $kT \sim \Delta$ in a wide range of temperatures excluding high temperatures (relative to 100 K).

At high hydrostatic pressures the off-center well gradually disappears as a consequence of a decrease in the lattice constant. Therefore the

TO(γ) line intensifies while the intensity of TO(β) decreases. Shand *et al.*[6] observed this phenomenon at 77 K applying pressures up to 32 kbars. According to the present model, the effect of pressure on the TO(β)-TO(γ) intensity ratio is expected to be more significant at lower temperature where the variation of Δ with pressure is more critical for lowering the off-center wells population. It is worthwhile mentioning that in the case of KCl:Li$^+$, where off-center sites are still populated at 2 K, it was predicted that hydrostatic pressure of 7 kbars should be sufficient to shift the Li$^+$ to the center. This was actually observed by Kahan *et al.*[37]

The application of pressure does not only change Δ but also moves the off-center well minimum towards the center. This may decrease the covalency and as a result $I_{\mathrm{LO}(\beta)}/I_{\mathrm{TO}(\beta)}$ ratio should increase. Shand *et al.*[1] observed a relative increase of LO(β) as function of pressure at moderate pressures (up to 7 kbars). When pressure is further increased, LO(β) should decrease as well, due to the decrease in the off-center population. The effect of pressure is further discussed in connection with mixed Cu halides in the following paper.[31]

B. CuCl, $\vec{k} \neq 0$ phonons

In Sec. II the relation between the correlation length and the neutron scattering intensity was derived; the shorter the correlation length the lower should be the intensity. In order to discuss the measured inelastic neutron scattering intensity anomalies,[10,11] we first summarize the conclusions of Sec. II: (i) The correlation length is expected to be shorter for phonons involving off-center Cu$^+$ than for those involving central Cu$^+$, when a similar type of vibration is considered. (ii) The correlation length decreases with increasing $|\vec{k}|$. (iii) Among the various modes, those for which the relative participation of Cu$^+$ in the vibration is larger than that of the Cl$^-$, will experience a shorter correlation length. (iv) For a certain phonon branch, the correlation length (in ZB structure) is anticipated to decrease from [111] to [100], being the shortest for the [110] direction. Following these conclusions the anomalies of the inelastic neutron scattering experimental data will be interpreted by means of the proposed model. It is important to note that a decrease in the correlation length may be observed experimentally only when it is critically short, namely, at the range where the phonon line drastically broadens.

We shall start with the vibrations in which off-center Cu$^+$ participate. The acoustical branches are not expected to be resolved from the corresponding ones in which central Cu$^+$ participate (one-mode behavior of the acoustical phonons[31]). LO(β) appears with low intensity in Raman at $\vec{k} \approx 0$ and therefore the probability of detecting this line at larger wave vectors is extremely small. This line was not searched for in neutron scattering experiments. TO(β) was recently observed at 4.2 K in the [111] direction[10,28] and its intensity decreases as $|\vec{k}|$ increases and smears out at about half the Brillouin zone in that direction (see Fig. 4). This behavior is expected because of the decrease in the correlation length with $|\vec{k}|$. Moreover it is predicted that if looked for in the other symmetry directions, TO(β) will be seen to disappear at shorter wave vectors.

Phonons involving only central Cu$^+$ generally have a correlation length long enough not to be seriously affected as function of $|\vec{k}|$. This is the case for the optical γ modes. On the other hand, the acoustical branches exhibit a one-mode behavior in which both central and off-center Cu$^+$ participate. Therefore their correlation length is expected to be smaller. The LA phonon eigenvector calculated by lattice dynamical model shows that this vibration is mainly that of the Cu$^+$ ions, while Cl$^-$ hardly participate in it.[11] Therefore, the correlation length of this phonon is shorter than that of the TA phonons at any given $\vec{k}$. Out of all the symmetry directions the shortest correlation length will occur in the [110] direction. The higher the $|\vec{k}|$ in this direction the shorter the correlation length and thus the lower is the intensity. When the temperature increases the correlation length decreases. This explains the peculiar behavior of the LA phonon branch in the [110] direction recently observed by neutron scattering.[11] At low temperatures no anomaly was found. As temperature increases the intensity decreases starting from the *K* zone-boundary point. At 210 K the LA phonon at the *K* point totally smears out and the lower the wave vector in this direction the higher is the LA phonon intensity.[11] An interpretation of the anomalous behavior of TO(β) and LA(Σ) phonons in neutron scattering has not been given before. More neutron scattering experimental data is highly desirable. This concerns mainly the TO(β) in the [110] direction and LA in the [100] direction, both as function of temperature.

C. CuBr and CuI

Compared to CuCl, there is not as much information available on CuBr and CuI. In CuBr at room temperature two broad peaks are observed at optical frequencies (see Fig. 2): one is located at 161 cm^{-1} and is considered to be LO(γ), the other is located around 115 cm^{-1} and splits into two main peaks at lower temperature (see Fig. 2). A linear extrapolation of TO(γ) from lower temperature data yields $\omega[\mathrm{TO}(\gamma)] = 124$ cm^{-1} at room temperature.[13,56] Moreover, a careful analysis of the room-temperature Raman data (in terms of the reduced Raman spectrum[31]) reveals two peaks at 111 and 124 cm^{-1}. Both are infrared active[29] and show the same polarization dependence.[13,28] The CuBr optical phonon observed line frequencies are therefore assigned as follows: $\omega[\mathrm{TO}(\beta)]=111$ cm^{-1}, $\omega[\mathrm{TO}(\gamma)]=124$ cm^{-1}, and $\omega[\mathrm{LO}(\gamma)]=161$ cm^{-1}.

If one uses just the $\omega[\mathrm{TO}(\gamma)]=124$ cm^{-1} and $\omega[\mathrm{LO}(\gamma)]=161$ cm^{-1} in the LST relation, $\epsilon_0/\epsilon_\infty=1.69$ is yielded, compared with 1.96 ($\epsilon_0=7.95$, $\epsilon_\infty=4.06$) measured by Turner *et al.*[12] This discrepancy is too large in order to be accepted. Moreover, at 90 K where the off-center Cu$^+$ population is much smaller [TO(β) is supressed] $\epsilon_0/\epsilon_\infty=1.55$ $\{\omega[\mathrm{TO}(\gamma)]=134$ cm^{-1}, $\omega[\mathrm{LO}(\gamma)]=167$ cm$^{-1}\}$ is in excellent agreement with 1.55 which was measured directly.[12] It is therefore clear that two oscillators contribute to the dielectric response at 300 K and mainly one at $T=90$ K. Repeating the procedure used for CuCl—using the reduced Raman intensities ratio along with $\epsilon(161\ \mathrm{cm}^{-1})=0$—the values of $S_\beta=2.7$ and $S_\gamma=1.1$ are obtained for 300 K. $\epsilon_0=\epsilon_\infty+S_\gamma+S_\beta=7.9$ is in an excellent agreement with 7.95 measured by Turner *et al.*[12] The other zero of $\epsilon(\omega)$ comes out at 119 cm^{-1} which is believed to be the LO(β) frequency.

Then

$$\frac{\epsilon_0}{\epsilon_\infty}=\left(\frac{\omega[\mathrm{LO}(\beta)]\omega[\mathrm{LO}(\gamma)]}{\omega[\mathrm{TO}(\beta)]\omega[\mathrm{TO}(\gamma)]}\right)^2=1.94$$

compared with 1.96 at 300 K. It will be very interesting to compare a direct measurement of polaritons dispersion at 300 °C with relation $c^2q^2/\omega^2=\epsilon(\omega)$ where both oscillators contributes to $\epsilon(\omega)$.

LO(β) cannot be inferred from ir measurements[29] because of the frequency proximity of the two oscillators. LO(β) cannot be seen in Raman due to its low intensity especially relative to the strong neighboring TO(γ). Both TO(β) and TO(γ) do show the same polarization dependence. Moreover, at room temperature TO(β) is more intense that TO(γ) while the opposite is true at low temperature.

The previous assignment of what we call here TO(β), was LO-TA at X or L symmetry points.[12,13,28] The intensity temperature dependence of this line is much stronger than that anticipated theoretically for this combination. Also its temperature-dependent frequency shift[28] is larger than the shift deduced from neutron scattering data[57,58] for such a combination. Moreover one would expect a similar combination to occur in other Cu halides as well, but such a line was not observed.[3] In our model based on two kinds of potential minima having an energy difference Δ, CuBr is an example of a case where $\Delta > kT$, for temperatures below 200 K. This condition yields an exponential T dependence of the off-center copper population below 200 K and therefore a similar T dependence of the TO(β) intensity, as was actually observed.

The population decrease of the off-center Cu$^+$ with temperature was deduced from the Bragg neutron scattering data using the anharmonic model.[36] The anharmonic model and the disorder model yield the same results for small off-center population or for short off-center distance r_0.[15] Stern and co-workers are presently studying CuBr by EXAFS (extended x-ray absorption fine structure). They have observed[59] a very large temperature dependence at low temperatures, which corresponds to a big decrease in the disorder of the copper sites in CuBr. From the data one may obtain a clearer picture as to the amount of disorder and the distance r_0 of the off-center sites.

In CuI only one TO line is resolved at room temperature.[3,31] This seems to be consistent with the conclusion drawn from the intensity temperature dependence of x-ray Bragg reflections.[16] The Raman spectrum smears at higher temperature.

It is interesting to note that in a very recent study[14] it has been observed that at 100 °C an extra line begins to build up in the Raman spectra between 70 and 100 cm^{-1}. This line was interpreted[14] similarly to that presented here, namely, belongs to off-center Cu$^+$ vibrations.

D. General discussion

In the previous sections it was demonstrated how the available experimental data of Cu halides can be interpreted in terms of the dynamical model proposed. In spite of this, it would be advantageous if more direct techniques, such as EXAFS,[59,60] were used in order to prove not only the existence of the four off-center potential minima, but also to measure their distances from the center, and the tunneling rate among them.[60] Once this is achieved, the exact shape of the Raman TO(β)-TO(γ) region can be fitted using the off-center polarization derivatives and their well's minima shapes, as adjustable parameters. At present, it seems clear that this model gives a consistent qualitative interpretation of the experimental data. In particular it provides an explanation for the existence of the LO(β) line, the polaritons' dispersion, the resonance Raman data, the neutron scattering data together with the T dependence of the Bragg x-ray and neutron scattering intensity; all these were not explained by previous models.

The two previous models[2,3] do reproduce the Raman spectrum of the $\vec{k}\approx 0$ TO(β)-TO(γ) frequency range only in CuCl and excluding the LO(β) line.[1] These models are based on a Ruvalds-Zawadowski[61] type of interaction between the TO phonon and a background of two phonon combinations of acoustical branches. One model is fitted to the

Raman spectrum at 40 K using several parameters,[2] and is also able to reproduce the pressure-induced spectrum at this temperature[1] and to adjust the LST relation.[2] The second model[3] tries to fit the Raman spectra at various temperatures, but the physical meaning of the parameter temperature dependence is not quite understood.[3] There is also a discrepancy between the two models concerning the frequency of the singularity in the two-phonon density of states. While it is 170 cm^{-1} in the first model[2] it is assumed to be at 146 cm^{-1} in the second.[3]

It should also be noted that in order to estimate the V_3^{LO} (the third-order anharmonic interaction),[2] one has to consider the total intensity at the TO frequency range, in the LO geometry presented in Refs. 2 and 7. It was argued before that this intensity cannot be due to internal reflection,[7] or due to a second-order process [because of zero intensity in a $z(xx)\bar{z}$ geometry[7]]. But when this total LO geometry intensity is taken into account, the $(V_3^{\mathrm{TO}})^2/(V_3^{\mathrm{LO}})^2$ value would have turned out to be much less than unity.[2] Another question that arises in connection with these models is the total disappearance of the β optical phonon in the mixed crystal system $\mathrm{CuCl}_{1-x}\mathrm{Br}_x$ with small x. Murahashi *et al.*[62] have measured the infrared absorption in thin films of $\mathrm{CuCl}_{0.9}\mathrm{Br}_{0.1}$ and $\mathrm{CuCl}_{0.85}\mathrm{Br}_{0.15}$ at 2 K. In both mixtures the "extra" β line vanishes. The small Br concentration may not be sufficient to shift the frequency of the "true TO" $\vec{k}=0$ mode beyond the P_3 singularity region or to drastically reduce the coupling (CuBr is known to be also very anharmonic[24]). Even then, a contribution of the "extra" phonon in the absorption is expected, but was not detected.[62]

According to these models, when the "true TO" is compelled from the region of interaction by the application of hydrostatic pressure,[6] a change in the Grüneisen parameter is expected from $\gamma = 1.9$ of the TO(γ) line below 19 kbars to $\gamma = 2.4$ above that pressure, as figured out for the "true TO."[1] Such a change was not detected.[6] Furthermore, at small $\vec{k}$ (polariton region) the "true TO" is expected to move to a much lower frequency and put far off the interaction region.[6] In this case just one polariton dispersion curve should have been seen. Instead, two distinct polariton dispersion curves, β and γ, were observed[52] (Fig. 5); both results are consistent with the present model.

The two models mentioned above are based on the high anharmonicity observed in CuCl. A secondary potential minimum as assumed in our model will result also in high anharmonicity that will be observed in both central and off-center Cu^+ vibrations. This may cause interaction between TO(β) and TO(γ) that is not included in the present discussion. Moreover, such high anharmonicity may be the cause of the asymmetry observed in the LO(γ) line of pure CuBr even at very low temperature.[31]

Our assertion is that CuCl, although a prominent member of the Cu-halides group, is not unique with respect to phonon anomalies. Similar phonon anomalies are observed in CuBr and CuI as well, but start at higher temperatures than in CuCl. We do find a systematic trend that follows the same course found in x-ray and neutron scattering data. Also the observability of both Raman and neutron scattering spectra is in line with these findings. The same trend is observed also in the mixed Cu-halide crystals with respect to the unusual high intensity of the disorder-induced TA modes and its temperature dependence. This will be presented and discussed in the following paper.[31] Unusual properties similar to those of Cu-halides are also found in related compounds, such as AgI,[63] that will be reported separately.

IV. SUMMARY

Our model for Cu halides assumes the possibility of secondary four equivalent minima in the copper ion potential, in addition to the potential minimum of the copper ion at the ideal (central) site. These off-center wells are probably due to the energy proximity of the Cu 3*d* and 4*s* electronic shells, yielding an additional covalent attractive potential between the Cu 3*d* and the halogen *p* electrons. It is assumed that the tunneling rate of the copper among the four off-center sites is larger than that between central and off-center sites and produces an off-center Cu^+ tunneling state. The off-center Cu^+ population is temperature and pressure dependent via the potential difference Δ between off-center and central well minima.

In relation to phonons, this system may be described as having a two-mode behavior of the optical vibrations at $\vec{k}\approx 0$; one is due to Cu^+ at the ideal positions (γ) and the other is due to Cu^+ at the off-center tunneling states (β). The correlation length of the off-center phonons is shorter than that of the central phonons, but is assumed to be long enough at $\vec{k}\approx 0$ such that the relaxation of the polarization selection rules can be considered as a perturbation. In this case each type of vibration (β and γ) exhibits the same symmetry T_2 at $\vec{k}\approx 0$, but has a different set of force constants. This explains the appearance and properties of the "extra" TO(β) and LO(β) in the Raman and infrared spectra. Consequently the polariton dispersion and the resonance Raman data in CuCl can readily be understood. In addition, this model accounts for the temperature and pressure dependence of the optical phonon line intensities in Cu halides.

The correlation length decreasing with $|\vec{k}|$, explains the $|\vec{k}|$ dependence of the TO(β) intensity in CuCl, measured by inelastic neutron scattering at 4.2 K. The $\vec{k}$ and T dependence of the LA branch in the [110] direction is explained in a similar way.

The present conclusions are consistent with those deduced from the intensity temperature dependence of Bragg x-ray and neutron scattering data. The trend found with respect to the temperature of the off-center population onset in Cu halides agrees with that found here for many of the phonon characteristics. This trend is an integral part of our model.

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