

## Quantitative approach to the off-center model in CuCl

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We use a model potential which includes the Madelung and van der Waals attraction and the Born-Mayer-Verwey repulsion to obtain a quantitative estimate of the vibrational and structural properties of CuCl at different temperatures and hydrostatic pressures. To achieve this goal we gather and use all relevant experimental data including our new temperature-dependent phonon-polariton measurements. We obtain a double-well potential which is able to reproduce the vibrational anomalies as observed by Raman scattering, infrared, and phonon-polariton measurements. The structural implications of the model are discussed and compared with extended x-ray absorption fine-structure and x-ray- and neutron-diffraction results. Our approach is valid also for the other Cu halides as well as for AgI for which data less extensive than those available for CuCl can be found.

### I. INTRODUCTION

CuCl has received much attention in recent years because of a great number of extraordinary properties. Together with CuBr, CuI, and AgI, it exhibits an ionic conductive phase at high temperature (for a review see Ref. 1). In this phase it is commonly accepted that the cations occupy a great number of sites in the cell defined by the anions; in extreme cases they are even treated as a liquid which fills up the anion matrix. At a low enough temperature Cu halides exhibit the zinc-blende ( $T_d^2$ ) structure and this is a nonconducting phase. In this phase a variety of anomalies are known to exist and they are especially pronounced in the phonon spectrum: this was thoroughly reviewed by Vardeny and Brafman.<sup>2</sup> While the models which have been proposed earlier<sup>3-5</sup> were limited to the optical phonon spectrum of CuCl only, the off-center model proposed by Vardeny and Brafman in Ref. 2 was able to account also for the irregular phenomena observed in the Raman spectra of CuBr, CuI,<sup>2-6</sup> and AgI,<sup>7</sup> as well as of the mixed Cu halides<sup>8,9</sup> and  $\text{Cu}_x\text{Ag}_{1-x}\text{I}$ .<sup>10</sup> Here we shall present a quantitative approach to the off-center model in CuCl: Calculations which allow for the existence of a cation potential having additional minima. We shall derive the frequencies of the corresponding phonons in CuCl as well as the position of the cation at off-center as a function of temperature (0–300 K) and hydrostatic pressure (up to 32 kbar). The organization of this paper is as follows. We start by reviewing and critically comparing the main relevant experimental results (including new ones) which show anomalies in the optical phonon spectrum of CuCl. These will include Raman scattering, neutron scattering, infrared and polariton measurements. Section III is devoted to structural anomalies as found by x-ray and neutron diffraction and extended x-ray-absorption fine structure (EXAFS), and the way they were explained. A review of the main theoretical models with emphasis on the off-center model is given in Sec. IV. In Sec. V we present the details of the model potential. The assumptions made and the results obtained are com-

pared to experiment as well as to other calculations. The conclusions are given in Sec. VI.

### II. ANOMALIES IN THE OPTICAL PHONON SPECTRUM OF CuCl: REVIEW OF EXPERIMENTAL RESULTS

Group theory predicts for the zinc-blende ( $T_d^2$ ) structure of CuCl a single optical-phonon branch, labeled  $\gamma$ , split into  $\text{TO}(\gamma)$  and  $\text{LO}(\gamma)$ . However, an additional  $\mathbf{k}=0$  mode has been observed by Raman scattering (see Ref. 2 for extensive references), inelastic neutron scattering,<sup>11,12</sup> infrared absorption,<sup>13-15</sup> and reflection,<sup>13,16</sup> as well as polariton dispersion.<sup>6,9,17,18</sup> This mode is obviously a polar mode and is labeled here by  $\beta$ ,  $\text{TO}(\beta)$  and  $\text{LO}(\beta)$ . In the following we briefly review these results, and compare them with similar anomalies observed in the other Cu halides or in AgI.

#### A. Raman scattering

At temperatures down to 2 K a broad and intense  $\text{TO}(\beta)$  line is observed in the spectra, while  $\text{LO}(\beta)$  is weak and may only be resolved at the lowest temperatures (see Fig. 1). An increase in temperature causes the broadening of all the lines, indicating the high degree of anharmonicity of the crystal. The frequencies of the extra  $\beta$  lines are more sensitive to changes in temperature than those of the normal  $\gamma$  lines.<sup>5,19,20</sup> Neither the intensity of  $\text{TO}(\beta)$  nor that of  $\text{TO}(\gamma)$  follow the Bose ( $n+1$ ) temperature dependence, though the combined area under the peaks does show this kind of temperature dependence.<sup>2,19-21</sup> Hydrostatic pressure applied at liquid- $\text{N}_2$  temperature drastically reduces the  $\text{TO}(\beta)$  intensity. The frequencies of the  $\gamma$  lines increase with increasing pressure, while that of  $\text{TO}(\beta)$  does not change much.<sup>22</sup> A similar  $\beta$  mode was found also in the Raman spectra of CuBr,<sup>6</sup> while in AgI two modes,  $\beta_1$  and  $\beta_2$ , were found on top of the symmetry allowed spectrum [the low-temperature stable phase of AgI is wurzite (Ref. 7 and references therein)].

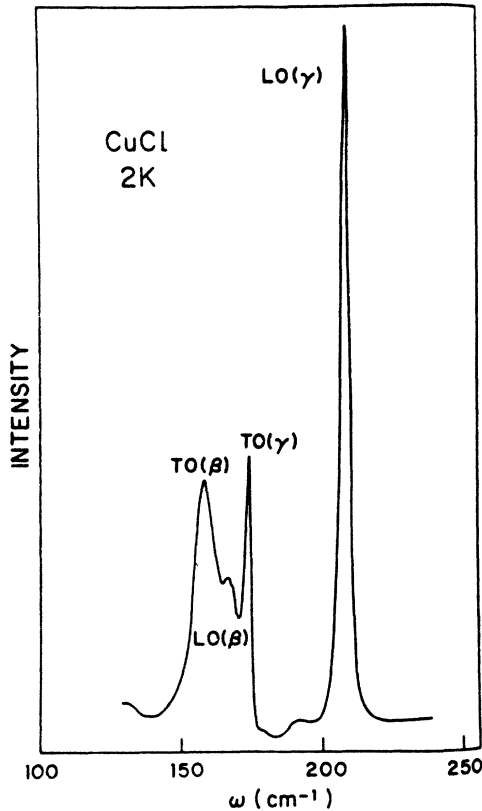


FIG. 1. The Raman spectrum of CuCl at  $T=4$  K.

An additional low-frequency line, labeled  $d$ , was observed in the Raman spectrum of all the Cu halides. This line is very much enhanced in the spectra of the mixed crystals<sup>8</sup> and was interpreted as a disorder-induced TA mode. The appearance of this forbidden mode in the spectra of the pure crystals indicates that a high degree of disorder is present in these crystals even without mixing.

### B. Neutron inelastic scattering

The  $\text{TO}(\beta)$  line has been studied by neutron inelastic scattering only in CuCl and only at liquid-He temperature.<sup>11,12</sup> Its intensity is strongly  $\mathbf{k}$  dependent, while at  $\mathbf{k} \approx 0$  it is comparable to that of the  $\text{TO}(\gamma)$  line; it decreases gradually at larger  $\mathbf{k}$  in the [111] direction, until it smears out at  $\mathbf{k}$  approaching about half of the Brillouin zone.<sup>11</sup> Similar behavior was observed at different  $\mathbf{k}$  directions as well.<sup>12</sup>

### C. Infrared and phonon polariton measurements

These two different measurements are essentially probing the same frequency-dependent dielectric function  $\epsilon(\omega)$ . In the case of infrared (ir) reflectivity one considers the complex dielectric function given by the following expression:

$$\epsilon(\omega) = \epsilon_{\infty} + \sum_{j=1}^n \frac{s_j \omega_j^2}{\omega_j^2 - \omega^2 - i\omega\gamma_j}, \quad (2.1)$$

where  $\epsilon_{\infty}$  is the high-frequency dielectric constant,  $\omega_j$  are the transverse optical-phonon frequencies of the  $n$  dif-

ferent vibrations present in the crystal, and  $s_j$  and  $\gamma_j$  are their oscillator strengths and damping constants, respectively. The frequency dependent reflectivity is given by

$$R(\omega) = \left| \frac{\sqrt{\epsilon(\omega)} - 1}{\sqrt{\epsilon(\omega)} + 1} \right|^2. \quad (2.2)$$

On the other hand, the phonon-polariton dispersion is given by

$$cq(\omega) = \omega \sqrt{\epsilon(\omega)}, \quad (2.3)$$

where  $\epsilon(\omega)$  is the real dielectric function (for undamped oscillators  $\gamma_j=0$ ). When analyzing the ir data one fits the theoretical expression (2.2) to the measured  $R(\omega)$ , while  $\text{TO}(j)$ ,  $s_j$ , and  $\gamma_j$  are parameters. In the analysis of the polariton results, one fits Eq. (2.3) to the experimentally measured dispersion, where the only parameters are  $s_j$ . Undoubtedly, the oscillator strengths  $s_j$  obtained by the two methods have to agree.

The phonon-polariton dispersion has been measured in the temperature range 2–300 K in all Cu halides<sup>6,9</sup> and in AgI.<sup>7</sup> In CuCl it was fitted using two oscillators,  $\beta$  and  $\gamma$ , with temperature-dependent oscillator strengths,  $s_{\beta}(T)$  and  $s_{\gamma}(T)$ . In CuBr the  $\beta$  mode was detected only at temperatures higher than 77 K (Ref. 6) while in CuI only the  $\gamma$  mode was observed at temperatures up to 300 K. The contribution of *two* extra modes,  $\beta_1$  and  $\beta_2$ , in addition to

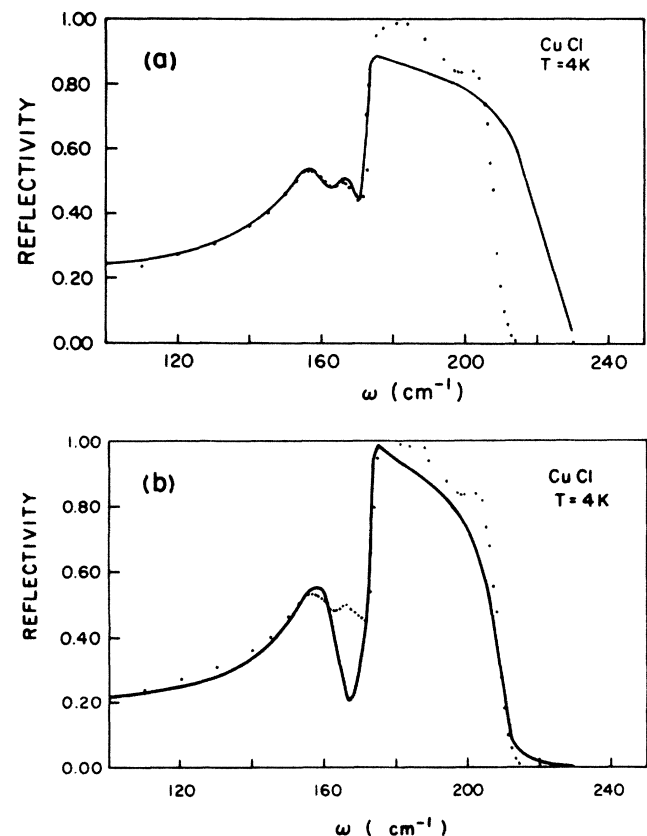


FIG. 2. The ir reflectivity of CuCl at  $T=2$  K. Dots: experimental values (Ref. 16). Solid curve: (a) calculated using the parameters reported by Namba *et al.* (Ref. 16) and (b) our parameters.

TABLE I. Parameters obtained by Nanba *et al.* (Ref. 16) from their ir reflectivity results in CuCl at 2 K.

| Mode of vibration<br>$j$ | TO( $j$ )<br>( $\text{cm}^{-1}$ ) | LO( $j$ )<br>( $\text{cm}^{-1}$ ) | $s_j$ | $\gamma_j$<br>( $\text{cm}^{-1}$ ) |
|--------------------------|-----------------------------------|-----------------------------------|-------|------------------------------------|
| 1                        | 155.7                             | 166.5                             | 1.49  | 10                                 |
| 2                        | 166.5                             | 171                               | 1.02  | 11.5                               |
| 3                        | 173.3                             | 223.8                             | 0.59  | 1.02                               |

the  $\gamma$  mode was necessary for fitting the polariton dispersion in AgI.

Infrared measurements in CuCl (Refs. 13–16) also revealed the additional  $\beta$  mode at liquid-He temperatures, and followed its unusual evolution when the temperature was raised. The  $\beta$  mode was also observed in CuBr but at higher temperatures,<sup>13</sup> while in AgI both  $\beta_1$  and  $\beta_2$  were observed at room temperature.<sup>23</sup> Though a large number of ir reflection spectra have been reported, the fit to the theoretical  $R(\omega)$  has been done only in CuCl at 2 K by Nanba *et al.*,<sup>16</sup> where *three reflection bands* were observed and therefore *three oscillators* were used for the fit. In Fig. 2(a) we have reproduced the results of Nanba *et al.*,<sup>16</sup> together with the  $R(\omega)$  curve calculated using their parameters (listed in Table I); this full fit was not presented in Ref. 16. Although the low-frequency spectrum is very well reproduced, one can see that  $R(\omega)$  does not fit the measured reflectivity in the high-frequency range, which is the most significant part of the spectrum. We have recalculated  $R(\omega)$  using the oscillator strengths and the TO frequencies obtained from the polariton-dispersion fit<sup>6,9</sup> with the parameters listed in Table II. In Fig. 2(b) we present this curve along with the same experimental points of Nanba *et al.* Our curve fits well the main features of the measured reflectivity but cannot reproduce, of course, the structures around 170 and 190  $\text{cm}^{-1}$ . These two weak features were dealt with differently in Nanba's analysis despite their similar intensities. The peak around 170  $\text{cm}^{-1}$ , which was observed also in the reflectivity spectra of Plendl *et al.*<sup>13</sup> and has a counterpart in the transmissivity spectra of Ikezawa,<sup>14</sup> has been explicitly taken into account in Nanba's analysis, while the other one has been neglected. We assert that both these features may be due to surface effects and are not intrinsic proper-

TABLE II. Parameters used in this work to calculate the ir reflectivity of CuCl at 2 K measured by Nanba *et al.* (Ref. 16). TO( $j$ ) and  $s_j$  from our polariton dispersion fit (Refs. 6 and 9). Only the damping constants have been adjusted to fit the ir results.

| Mode of vibration<br>$j$ | TO( $j$ )<br>( $\text{cm}^{-1}$ ) | LO( $j$ )<br>( $\text{cm}^{-1}$ ) | $s_j$ | $\gamma_j$<br>( $\text{cm}^{-1}$ ) |
|--------------------------|-----------------------------------|-----------------------------------|-------|------------------------------------|
| 1( $\beta$ )             | 155                               | 166.5                             | 1.7   | 10.7                               |
| 2( $\gamma$ )            | 174                               | 208                               | 0.7   | 0.05                               |

TABLE III. Parameters used to calculate the ir reflectivity of AgI at 300 K measured by Bruesch *et al.* (Ref. 23). TO( $j$ ) and  $s(j)$  from the polariton dispersion fit of Brafman and Vardeny (Ref. 7). Only the  $\gamma_j$  were adjusted to fit the ir results.

| Mode of vibration<br>$j$ | TO( $j$ )<br>( $\text{cm}^{-1}$ ) | LO( $j$ )<br>( $\text{cm}^{-1}$ ) | $s_j$ | $\gamma_j$<br>( $\text{cm}^{-1}$ ) |
|--------------------------|-----------------------------------|-----------------------------------|-------|------------------------------------|
| 1( $\beta_1$ )           | 39                                | 41                                | 0.4   | 14                                 |
| 2( $\beta_2$ )           | 83                                | 91                                | 1.1   | 21                                 |
| 3( $\gamma$ )            | 104.6                             | 124                               | 1.2   | 22                                 |

ties of the crystal. We therefore conclude that there are only two oscillators in CuCl at all temperatures down to 2 K.

We have used the same procedure in the case of AgI: we have computed  $R(\omega)$  using the oscillator strengths obtained from polariton measurements of Brafman and Vardeny<sup>7</sup> and have compared it to the experimental ir reflectivity measured by Bruesch *et al.*<sup>23</sup> (see Table III); the excellent fit obtained is shown in Fig. 3.

### III. STRUCTURAL ANOMALIES

From the x-ray and neutron-diffraction investigations<sup>1,24–27</sup> it appears that the Cu halides, as well as AgI, exhibit “structural disorder.”<sup>27</sup> Although the zinc-blende structure is established as the low-temperature phase of the Cu halides, analysis of the integrated intensities invariably yields unusually high values for the cation mean-square displacement  $\langle u^2 \rangle$  down to quite low temperatures: about 370 K in CuI,<sup>24</sup> 150 K in CuBr,<sup>24</sup> and 5 K in CuCl.<sup>27</sup> The data were equally well explained by two models. The first, the anharmonic model, assumes asymmetric anharmonic thermal vibrations of the Cu ions along the tetrahedral diagonals. The second one, the “disorder” model, assumes a statistical distribution of the copper ions among four metastable positions located on the [111] directions, toward the faces of the tetrahedron formed by the anions. Although this model allowed for

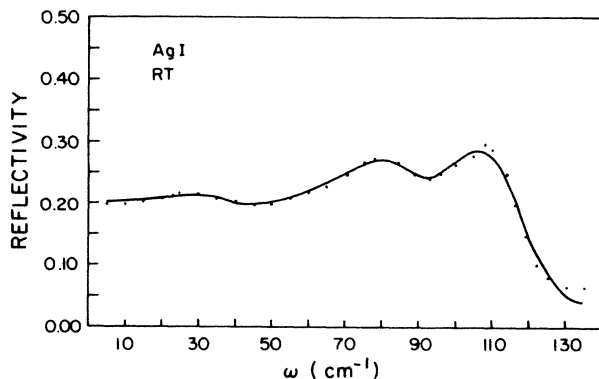


FIG. 3. The ir reflectivity of AgI at 300 K. Dots: experimental values (Ref. 23). Solid line: calculated using the parameters reported by Brafman and Vardeny (Ref. 7).

somewhat smaller  $\langle u^2 \rangle$  values for the Cu ions, it was criticized on the grounds that it is static and yields small displacements comparable to vibrational amplitudes.<sup>1</sup> Diffuse neutron scattering in CuCl (Ref. 27) also indicated that a statistical distribution of the Cu ions over the  $(z, z, z)$  equipoint will *not* give rise to the observed  $k$ -dependent diffuse background. It was suggested that "correlated displacements" should be considered. The Cu-Cu radial density function in CuCl was found to be much broader and less defined than that corresponding to Cl-Cl.

More recent and more direct evidence for structural anomalies in the Cu halides comes from EXAFS measurements.<sup>1,28</sup> Data on Cu halides and AgI from low temperatures (77 K) up into the superionic phase have been analyzed in terms of the "excluded volume" model.<sup>1</sup> According to this model, the anions are fixed at their lattice sites, while the cations may be found anywhere inside the unit cell, but not closer to the anions than a distance called  $r_{\text{excluded}}$ . The interpretation of the EXAFS data using this model does not reveal any anomalies as long as a phase transition is not approached. Their results indicate that the tetrahedral locations in the halogen lattice are preferred by the mobile cations at low temperature, with  $r_{\text{excluded}}$  approximately equal to the nearest-neighbor distance calculated from the lattice constant. As temperature increases,  $r_{\text{excluded}}$  decreases, allowing for the cation a larger volume around its ideal position. In the high-temperature conducting phase, this volume touches the faces of the tetrahedron in points which indicate the direction of the actual conduction path.

A more recent and very careful EXAFS analysis<sup>28</sup> of CuBr concluded that the data cannot be explained by the disorder model. The results were interpreted in terms of an anharmonic effective single-particle potential for the Cu ion, containing third- and fourth-order terms.

#### IV. ANOMALIES IN THE OPTICAL-PHONON SPECTRUM OF CuCl: THEORY

##### A. Anharmonic models

A number of models have been proposed in order to explain the phonon spectrum of CuCl. Krauzman *et al.*<sup>4</sup> viewed the entire  $\beta$ - $\gamma$  spectrum as arising from an anharmonic coupling between the "harmonic" TO and a two-phonon continuum. This continuum was supposed to terminate on its higher-frequency side with a  $P_3$ -type van Hove singularity which determined the shape of  $\beta$ - $\gamma$  spectrum at 40 K. They used five fitting parameters, two of them being  $\omega_{\text{TO}}$ , the frequency of the harmonic TO, and  $\omega_c$ , the frequency of the singularity ( $\omega_{\text{TO}} < \omega_c$ ).

The theory was employed by Shand *et al.*<sup>3</sup> in order to explain the Raman spectra at 40 K as a function of pressure. By allowing the parameters to change with pressure, they fitted their Raman spectra up to 6.8 kbar. Extrapolating the pressure dependence of  $\omega_c$  and  $\omega_{\text{TO}}$  they predicted that at a pressure of about 17 kbar  $\omega_{\text{TO}}$  will be greater than  $\omega_c$ , which means that it will be "pulled out" from the interaction region, so that only the harmonic TO will be left in the spectrum. Later measurements of Shand and Hanson<sup>22</sup> at pressures up to 32 kbar confirmed

qualitatively the transformation of the two-peak structure in the TO region into a single peak, but the change in the slope of  $\omega_{\text{TO}}$  versus pressure predicted by their model did not occur.

A similar model was proposed by Fukumoto *et al.*<sup>5</sup> and was fitted to the Raman spectra at different temperatures. The main disagreement between the two models is in the frequency of the singularity,  $\omega_c$ : while it is about 170  $\text{cm}^{-1}$  in the first model, it is assumed to be at 146  $\text{cm}^{-1}$  in the second one. However, the physics behind the temperature dependence of the parameters could not be explained.

##### B. The off-center model

The previous anharmonic models suffered from a lack of generality: their aim was to explain the TO( $\beta$ )-TO( $\gamma$ ) anomaly in CuCl only. A more general model inspired by the structural considerations mentioned before is the off-center model proposed by Vardeny and Brafman.<sup>2</sup> We first describe this model and we then show that it is able to account *qualitatively* for the available experimental data in CuCl, including our own polariton-dispersion measurements at different temperatures between 2 and 300 K.

The off-center model assumes that, in addition to the ideal sites in the lattice, the cations ( $\text{Cu}^+$ ) may occupy *four equivalent off-center sites in a tunneling state*. Namely, the existence of four equivalent secondary minima in

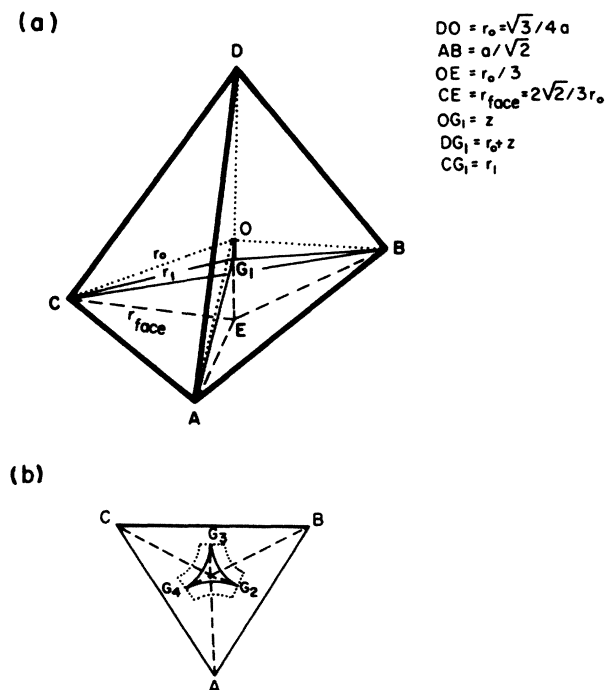


FIG. 4. (a) The cation in the tetrahedral cage formed by the anions.  $O$ : center.  $G_1$ : off-center. (b)  $G_2, G_3, G_4$ : projection of the possible tunneling orbit of the cation at a fixed  $z$ . Solid line:  $r_1$  is fixed. Dotted line:  $r_1$  is allowed to have a distribution with a finite width.

the  $\text{Cu}^+$  potential is postulated. They should be located along the [111] directions, toward the faces of the tetrahedron formed by the anions (points  $G_1-G_4$  in Fig. 4). Assuming that the tunneling rate between central and off-center sites is much lower than that among the displaced sites, one may define two different sublattices: one with  $\text{Cu}^+$  in ideal sites, and the other with  $\text{Cu}^+$  in the tunneling off-center states, both having the same  $T_d$  symmetry.<sup>2</sup> The cations at off-center sites would give rise to the  $\beta$  phonon, while in the  $\gamma$  mode the cations in the ideal positions would participate. This explains the appearance of the extra  $\beta$  phonon not only in CuCl, but also in CuBr, and does not exclude this from happening in CuI at sufficiently high temperatures. In AgI the  $\beta$  mode is then split into  $\beta_1$  and  $\beta_2$  as a consequence of the lower symmetry of the wurtzite structure.

The  $\beta$  phonon should have a shorter correlation length than the  $\gamma$  phonon.<sup>2</sup> This could explain why polarization selection rules are not properly obeyed in Raman scattering from CuCl and why  $\text{TO}(\beta)$  is so much broader than  $\text{TO}(\gamma)$  at low temperature. The correlation length of the  $\beta$  phonon decreasing with  $k$  explains the  $k$  dependence of the  $\text{TO}(\beta)$  intensity in CuCl, measured by inelastic neutron scattering. The off-center  $\text{Cu}^+$  ions act as phonon scattering centers, namely, these ions introduce disorder, which relaxes the selection rules and gives rise to new lines in the Raman spectrum.<sup>30</sup> The disorder induces the relatively weak  $d$  lines in the room-temperature spectra of the pure Cu halides which are assigned as TA modes. This assignment is further supported by the enhancement of this line in the spectra of the mixed Cu halides.

The relative population of the central (on) and off-center (off) sites is assumed to depend on the potential-energy difference  $\Delta$  of the respective minima. One may write

$$\frac{N_{\text{off}}}{N_{\text{on}}} = 4 \exp \left[ -\frac{\Delta}{kT} \right], \quad (4.1)$$

where the activation energy  $\Delta$  should be very sensitive to the interatomic distances. External factors, such as temperature and pressure, which affect the lattice constant, should also change  $\Delta$  and by that also the relative off-on population. On the other hand, the relative  $\text{TO}(\beta):\text{TO}(\gamma)$  Raman intensities, or the ratio of the two oscillator strengths  $s_\beta:s_\gamma$  are proportional to this relative population

$$I_{\text{TO}(\beta)}:I_{\text{TO}(\gamma)} \simeq s_\beta:s_\gamma \simeq N_{\text{off}}:N_{\text{on}}. \quad (4.2)$$

Therefore, once the ratio  $N_{\text{off}}:N_{\text{on}}$  is known,  $\Delta$  can be calculated. In the following we will discuss some of the parameters which affect  $\Delta$ . In Fig. 5 we have plotted the relative  $\beta$ - $\gamma$  intensities versus pressure as obtained from the spectra of Shand and Hanson,<sup>22</sup> along with the values calculated for  $\Delta$  at these pressures using Eqs. (4.1) and (4.2).  $\Delta$  is of the order of 10–20 meV, and slightly increases with pressure. In terms of the model this increase is readily understood: increasing pressure decreases the lattice constant, bringing atoms closer. This should result in an increase of repulsive interactions, thus an increase of energy barriers.

The other factor which affects  $\Delta$  is the temperature. In

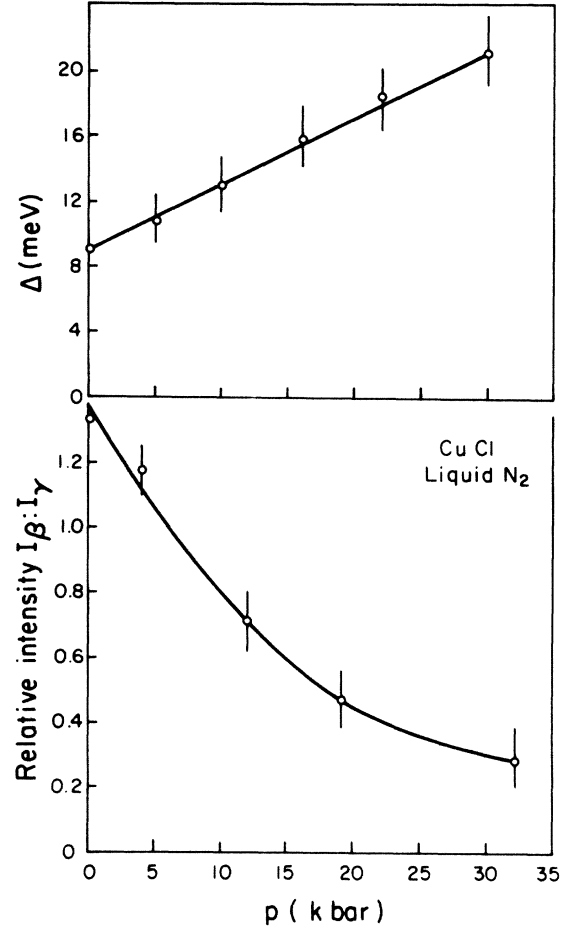


FIG 5. The relative intensities  $I_{\text{TO}(\beta)}:I_{\text{TO}(\gamma)}$  at different pressures measured from the Raman spectra of Shand and Hanson (Ref. 22) (lower). The values obtained for  $\Delta$  are also plotted as a function of pressure (upper). The solid lines drawn between the experimental points are only a guide to the eye.

order to analyze its influence on the relative off-on population we have relied on the ratio of the oscillator strengths  $s_\beta:s_\gamma$  obtained from polariton-dispersion measurements, which is by far more accurate than the intensity method used before. As polariton-dispersion measurements in CuCl were available only at 2 K, 80 K, and 300 K,<sup>6,9</sup> we measured the polariton dispersion at several additional temperatures between 2 and 300 K. The experimental technique was the same as described in Ref. 6. The values obtained for the two oscillator strengths are shown in Fig. 6(b), plotted against temperature. In Fig. 6(a) we plot the corresponding values of  $\Delta$ , calculated using Eqs. (4.1) and (4.2). The interpretation of the  $\Delta(T)$  dependence is not straightforward in this case. In the temperature region up to 80 K the linear thermal expansion coefficient of CuCl is negative,<sup>15</sup> which means that the interatomic distances decrease when the temperature is raised. According to the model, this should lead to higher energy barriers, which indeed happens:  $\Delta$  increases from a practically zero value at 2 K to almost 8 meV at 80 K. But for  $T > 80$  K the thermal expansion coefficient becomes positive and the lattice expands with increasing

temperature. Nevertheless,  $\Delta$  seems to keep growing and eventually saturates around room temperature (RT). There is more than one way to account for the fact that  $\Delta$  keeps increasing with  $T$  up to about 150 K despite the positive thermal expansion coefficient reported for temperatures above 80 K. One should not consider this problem in a naive manner in which  $\Delta$  is assumed to depend solely on the lattice parameter, especially when a change in temperature is involved. Temperature does not affect only the lattice parameter; it also increases the atom vibrational amplitudes and with it introduces anharmonicity. In this respect temperature dependence is not as clear an experiment as that of pressure dependence measured at a constant temperature, where a dependence on lattice parameter alone is a much better approximation as can be seen in Fig. 5. It should, however, be noted that the term responsible for the increase in the off-center population ( $\Delta/kT$ ) is constantly decreasing from about 1 around 80 K to about 0.6 around 30 K and this is reflected in the increase of  $S_\beta$  as seen in Fig. 6(b).

In order to complete the discussion we should mention some results obtained in the mixed crystals  $\text{CuCl}_{1-x}\text{Br}_x$  (Ref. 9) and  $\text{Cu}_x\text{Ag}_{1-x}\text{I}$ ,<sup>10</sup> which would illustrate how sensitive is the off-center phenomenon to changes in the immediate neighborhood of the  $\text{Cu}^+$  or  $\text{Ag}^+$  ions, respectively. In both cases for  $x=0$  (CuCl and AgI, respective-

ly) the crystals exhibit the extra  $\beta$  phonon at the temperature of measurement, while for  $x=1$  (CuBr and CuI, respectively) the phonon behavior is normal ( $\gamma$  phonons only). However, in both cases *very small amounts* of the normally behaved crystal are sufficient to alter the off-center modes of vibration. Polariton results in  $\text{CuCl}_{1-x}\text{Br}_x$  at 2 K (Ref. 9) could be explained assuming that the  $\text{Cu}^+$  ions occupy off-center sites if, and only if, all their neighbors are  $\text{Cl}^-$ . In the other case,  $\text{Cu}_x\text{Ag}_{1-x}\text{I}$ , at concentrations as low as  $x=0.05$ , the crystals already lose the wurtzite structure of pure AgI and become a mixture of polytypes. In this case the  $E_2$  lines which are characteristic of the wurtzite symmetry disappear from the Raman spectra. At the same time only *one* of the *two*  $\beta$  modes of pure AgI remains in  $\text{Cu}_{0.05}\text{Ag}_{0.95}\text{I}$ ,<sup>10</sup> similarly to the zinc-blende case of CuCl and CuBr. The corresponding value of  $\Delta$  increases from about 9 meV in AgI to about 17 meV in  $\text{Cu}_{0.05}\text{Ag}_{0.95}\text{I}$ , while the subsequent increase of  $\Delta$  with  $x$  is much smaller.

We shall conclude this discussion by asserting that the off-center model is able to explain *qualitatively* all the anomalies observed in the optical-phonon spectra of the Cu halides and AgI, as well as those of the mixed crystals  $\text{CuCl}_{1-x}\text{Br}_x$  and  $\text{Cu}_x\text{Ag}_{1-x}\text{I}$ .

In the following we shall demonstrate that this model may account also *quantitatively* for the anomalies discussed. We will look for the explicit form of the cation potential which may exhibit off-center minima. This potential should give the correct values for the  $k=0$  phonon frequencies,  $\omega_{\text{off}}$  and  $\omega_{\text{on}}$ , and for the corresponding values of  $\Delta$ , at different temperatures and pressures. It should also answer the intriguing questions: What is the actual position of the off-center cations and how does this position depend on temperature and pressure? Is it compatible with existing structure results?

## V. THE PROPOSED CATION POTENTIAL IN CuCl

### A. Off-center calculations: background

It is well known that  $\text{Cu}^+$  and  $\text{Ag}^+$  as impurities in alkali halides occupy off-center sites,<sup>31-37</sup> similarly to the  $\text{Li}^+$  (Refs. 31 and 34) and  $\text{F}^-$  (Ref. 31) ions. Whether the impurity ions will be found at on or off sites depends on the ion, on the nature of the host crystal, as well as on the interatomic distances. Hydrostatic pressure shifts the off-center ions toward the ideal, substitutional positions in the host lattice (center).<sup>33-34</sup> Theoretical calculations related to off-center ions were aimed to predict the equilibrium position of the impurity ion in a given host lattice. The method was to look for the *lowest-energy configuration* of the system host crystal plus one single impurity, and two basically different approaches were used in the calculations. The first one is semiclassical: Each ion carries a polarizable point charge (PPCI) and subjects to Born-Mayer repulsion.<sup>37,38</sup> The second<sup>34,39,40</sup> deals explicitly with the electronic processes involved in what the PPCI model calls "polarizability" of the  $\text{Cu}^+$  and  $\text{Ag}^+$  ions. The ground state of these ions is  $(n-1)d^{10}$ , with  $n=3$  for  $\text{Cu}^+$  and  $n=4$  for  $\text{Ag}^+$ . Their first excited state is  $(n-1)d^9ns^1$ . It is assumed in this second ap-

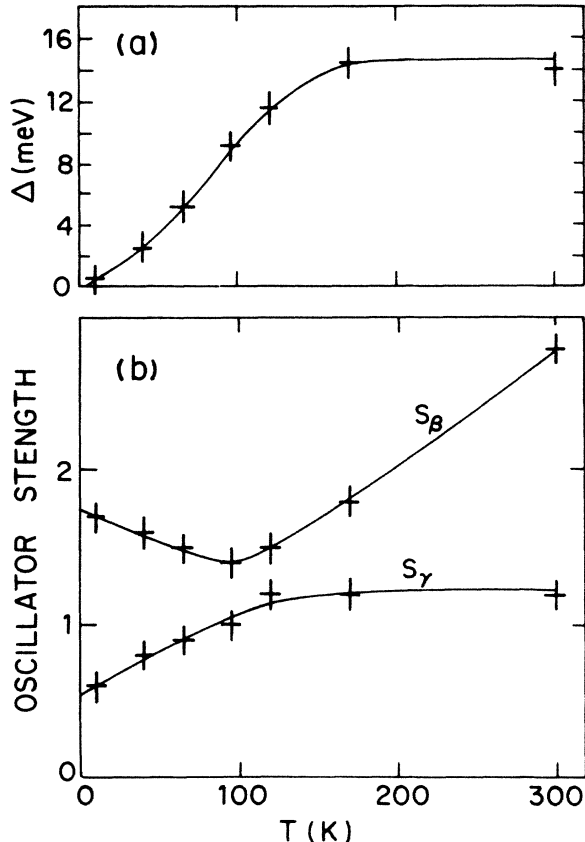


FIG. 6. The experimental temperature dependence of the oscillator strengths,  $s_\beta$  and  $s_\gamma$ , and of  $\Delta$ , as obtained from our polariton measurements. The lines are guides to the eye.

proach that there exists a higher lying charge transfer state  $(n-1)d^{10}ns^1$ , in which an electron from a neighboring anion is transferred to a metal ion [charge-transfer excitation (CTE)]. The resulting partial electron exchange leads to stronger binding between metal and halogen ions, and eventually to a central instability of the  $\text{Cu}^+$  and  $\text{Ag}^+$  ions.

No off-center calculations have been carried out for pure crystals, although a PPCI-type model has been developed for the treatment of the *motion* of the mobile ions through crystallographic tunnels in ionic conductors.<sup>41</sup> The results in AgI showed that there is a set of minimum energy paths which do not follow the center line of the tunnel, but deviate periodically. The question of the preferred *site* for the cations in structures with several types of sites that have apparently equivalent values of potential energy has been raised already then. It is our aim in the present work to treat the problem of cations occupying several equivalent sites in the lattice of a pure crystal.

### B. The proposed potential

We look for the potential  $U$  of the cation in one of its displaced sites which, according to the model, is assumed to be at a distance  $z$  from the center along the [111] direction towards one of the faces of the tetrahedron formed by the anions [ $G_1$  in Fig. 4(a)]. The high sensitivity of the off-center phenomenon to changes in the nature of the first neighbors or the distance to the first neighbors (see discussion in Sec. IV B) suggests the use of a cluster model, in which only the interaction with the first neighbors is taken into account. The potential  $U(z)$  is subjected to the following constraints.

(1) It reflects the geometrical tetrahedral surrounding

$$U(z) = U(r_0 + z) + 3U(r_1) \quad \text{where } r_1 = (r_0^2 - \frac{2}{3}r_0z + z^2)^{1/2}. \quad (5.1)$$

The tunneling state assumed by the model implies a finite probability of finding  $\text{Cu}^+$  also *in between* the  $G_1$ – $G_4$  points, which corresponds to a distribution of distances  $r_1$  [dotted curve in Fig. 4(b)]. As the displaced position approaches the face of the tetrahedron, i.e., when  $z$  increases, the width of this distribution should become larger allowing also for values  $r_1$  smaller than those given by the above formulas.

This would imply more terms in Eq. (5.1), corresponding to the different distances  $r_1$ . Since we are dealing here with short-range interactions decaying very fast with distance, the dominant terms would be those corresponding to the lowest allowed values of  $r_1$  and we shall keep only these terms in Eq. (5.1). The extent to which the minimum  $r_1$  differs from the expression written above depends on  $z$ . For very low  $z$  ( $z \rightarrow 0$ ) there should be practically no deviation from the [111] direction, while for higher  $z$  ( $z \rightarrow r_0/3$ ) the deviations from the [111] direction should become more significant. In order to avoid any explicit assumption concerning the shape of this distribution, and to make calculations simpler, we use a linear approximation for  $r_1$ , i.e., we neglect the  $z^2$  term in Eq.

(5.1). This approximation acts on  $r_1$  in the way we described before: it affects  $r_1$  less or not at all for  $z \rightarrow 0$  but becomes more significant for higher values of  $z$ .

(2)  $U(z)$  should have two minima: one for  $z=0$  (center) and one for  $z=r_{\text{off}}$  (off-center):

$$\left. \frac{dU}{dz} \right|_{z=0} = \left. \frac{dU}{dz} \right|_{z=r_{\text{off}}} = 0. \quad (5.2)$$

(3) The energy difference between these two minima should equal the measured  $\Delta$ :

$$U(r_{\text{off}}) - U(0) = \Delta. \quad (5.3)$$

(4) The calculated phonon frequencies

$$m\omega_{\text{on}}^2 = \left. \frac{d^2U}{dz^2} \right|_{z=0} \quad \text{and} \quad m\omega_{\text{off}}^2 = \left. \frac{d^2U}{dz^2} \right|_{z=r_{\text{off}}} \quad (5.4)$$

should equal the measured ones. Here  $\omega_{\text{on}}$  and  $\omega_{\text{off}}$  are the weighted mean values of the optical phonon frequencies:

$$\omega = \frac{1}{3}(2\omega_{\text{TO}} + \omega_{\text{LO}}).$$

Of course, the next and most difficult problem is to write the explicit form of the potential  $U(z)$ . We choose the PPCI approach taking into account the following interactions between spherical ions having radii  $r_+$  and  $r_-$  situated at a distance  $r$  apart.

(i) The Madelung term

$$U^C(r) = -\frac{\alpha_M e^*}{r} \quad (5.5)$$

with  $\alpha_M = 1.46$  for the zinc-blende structure<sup>42</sup> and  $e^* = 0.746e$  in accordance with the Phillips ionicity of  $\text{CuCl}$ .<sup>43</sup>

(ii) The van der Waals (vdW) interaction between polarizable ions. Since the additivity rule fails in all the Cu halides and AgI,<sup>44</sup> we are dealing with ions which overlap over a significant extent. For example, in  $\text{CuCl}$

$$r_+ + r_- = 0.96 \text{ \AA} + 1.81 \text{ \AA} = 2.77 \text{ \AA},$$

while the interatomic distance calculated from lattice constant is  $r_0 = 2.34 \text{ \AA}$ . Besides, there is an important contribution of the metal  $d$  electrons to the binding in  $\text{CuCl}$ ,<sup>44–47</sup> which leads to a hybridization of the halogen  $p$  and metallic  $d$  levels. It is impossible to make a distinction between the outermost electronic shells of the cation and anion, i.e., to define the extent of each ion. The simplest way to overcome this difficulty though a very crude approximation was to consider these ions as overlapping spheres, and to allow their polarizability to vary with the distance  $r$  between their centers. After Quigley and Das, we use a linear approximation for this dependence, but we allow both the anion *and* the cation polarizability to vary. The reason is that unlike  $\text{Li}^+$ , the  $\text{Cu}^+$  ion cannot be considered negligibly small with respect to  $\text{Cl}^-$ . Thus we write the polarizability of the cation (or anion) as

$$\alpha_+(r) = \begin{cases} 0, & r < r_+ \\ \frac{r-r_+}{r_0-r_+} \alpha_+, & r_+ < r < r_0 \\ \alpha_+, & r > r_0 \end{cases} \quad (5.6)$$

where  $\alpha_+$  or  $\alpha_-$  is a constant, the free-ion polarizability. So in the range of distances which we are interested in,  $r_- < r < r_0$ , the vdW interaction is

$$U^{\text{vdW}}(r) = - \frac{(r-r_+)(r-r_-)}{(r_0-r_+)(r_0-r_-)} \frac{C}{r^6}. \quad (5.7)$$

Here  $C$  is the vdW interaction constant. There is a wide spread in the values reported in the literature for this important constant in CuCl (Ref. 48 and 49) (see Table IV). The most recent values are 3–4 times larger than the early ones calculated by Mayer and Levy<sup>48</sup> and, as was pointed out in a recent review article by Shanker and Agrawal,<sup>50</sup> this holds also for other ionic crystals. In our calculations  $C$  was considered a fitting parameter. Since the “ionic radii” found in the tables are not representative of any specific crystal,<sup>44</sup> and since  $\text{Ag}^+$  and  $\text{Cu}^+$  are considered “highly deformable ions,” we have treated also  $r_+$  and  $r_-$  in Eq. (5.7) as parameters.

(iii) The Born-Mayer-Verwey (BMV) potential<sup>38</sup> was chosen for the repulsive interaction:

TABLE IV. The BMV constant  $A$  and the vdW constant  $C$  in CuCl.

|                                      | Mayer <sup>a</sup> | Bucher <sup>b</sup>    | This work |
|--------------------------------------|--------------------|------------------------|-----------|
| $A$ ( $\text{eV} \text{ \AA}^{12}$ ) | 6800               | 5312                   | 2875      |
| $C$ ( $\text{eV} \text{ \AA}^6$ )    | 91                 | 183 [ $R^{(2)}$ ]      | 1060      |
|                                      |                    | 1068 [ $s^2 R^{(2)}$ ] |           |

<sup>a</sup>Reference 48.

<sup>b</sup>Reference 44.

$$U^{\text{BMV}}(r) = \begin{cases} A_0 + \frac{A}{r^{12}}, & r \leq r_0 \\ b \exp\left[-\frac{r_+ + r_- - r}{\rho}\right], & r > r_0 \end{cases} \quad (5.8)$$

where the strength coefficient  $b$  and the hardness parameter  $\rho$  are usually obtained from fits to the experimental lattice constant and the bulk modulus of the crystal (Ref. 44 and references therein, and Ref. 48). The values of  $A$  and  $A_0$  which have to be used in our region of interest ( $r < r_0$ ) can be obtained from  $\rho$  and  $b$  by imposing continuity of the potential and of its slope at  $r_0$ . Since this is

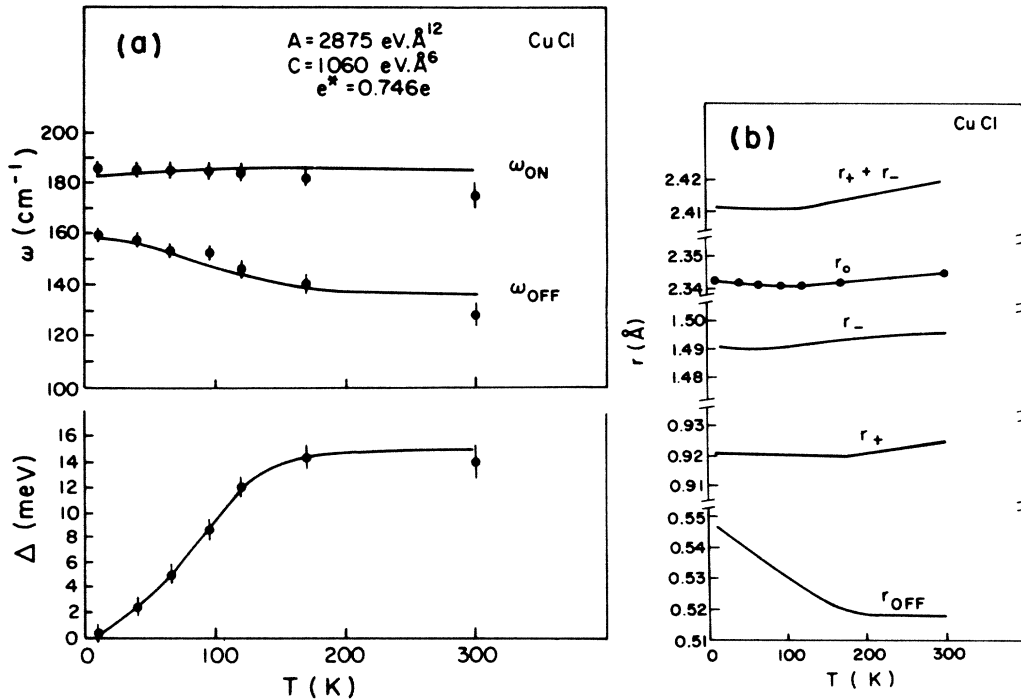


FIG. 7. (a) The temperature dependence of  $\omega_{\text{on}}$ ,  $\omega_{\text{off}}$  and  $\Delta$ . Points: experimental (our polariton measurements). Solid lines: calculated (the parameters are also indicated). (b) The temperature dependence of the ionic radii and their sum as compared to that of  $r_0$ . The calculated off-center position  $r_{\text{off}}$  is also plotted versus  $T$ .



quite an arbitrary constraint, we have regarded the quantities  $A$  and  $A_0$  also as parameters. In fact, only  $A$  enters the calculations, as one can see from Eqs. (5.1)–(5.4), thus it was the only parameter used in the calculation of the repulsive potential.

Finally these interactions are summarized:

$$U(r) = U^C(r) + U^{vdW}(r) + U^{BMV}(r). \quad (5.9)$$

After substituting (5.9) and (5.1) we obtain the potential of the cation

$$U(z) = U(A, C, r_+, r_-, z). \quad (5.10)$$

Here  $A$ ,  $C$ ,  $r_+$ , and  $r_-$  are parameters to be determined by fitting the values  $\omega_{on}$ ,  $\omega_{off}$  and  $\Delta$  calculated from Eqs. (5.4) and (5.3) to the measured ones at different temperatures and pressures. The changes induced in the potential by these external factors are taken into account via the expansion or the compression of the lattice:  $r_0(T)$  and  $r_0(p)$ .

### C. Application to CuCl

The experimental results to be used in the fit of the cation potential in CuCl are the phonon frequencies and  $\Delta$  at different temperatures [points in Fig. 7(a)] and different hydrostatic pressures [points in Fig. 8(a)]. While  $A$  and  $C$  are constants of the material, the ionic radii  $r_+$  and  $r_-$  are affected by changes in the lattice constant  $r_0$ : the experimental dependence of  $r_0$  on temperature and pressure has been reported [see Figs. 7(b) and 8(b), respectively]. Therefore the number of parameters seems to be quite large:  $r_+$  and  $r_-$  have to be changed for each set of  $\omega_{on}$ ,  $\omega_{off}$ , and  $\Delta$ . On the other hand, their magnitude is severely limited by Eq. (5.2) around  $r_+ = 0.92$  Å and  $r_- = 1.49$  Å. Equation (5.2) represents, in fact, the most distinctive feature of this potential: the fact that it contains *two* minima. In Fig. 9 we show the different shapes of  $U(z)$  obtained by slightly changing one of the ionic radii, say  $r_-$ . A decrease of 5% in its value leads to a purely attractive potential—the so called “polarization catastrophe,”<sup>38</sup> while an increase of about the same amount produces a steep increase of the repulsive interactions versus the attractive ones, which results in the disappearance of the second minimum of  $U(z)$ . The  $\Delta$  values are also extremely sensitive to  $r_+$  or  $r_-$ . The values which we obtained for  $r_+$  and  $r_-$  from our fit nicely follow the  $r_0(T)$  and  $r_0(p)$  functions.

The calculated values of  $\omega_{on}$ ,  $\omega_{off}$ , and  $\Delta$  are represented by solid lines in Figs. 7(a) and 8(a) and demonstrate the quality of the fit we are able to obtain. In both cases (when varying temperature or pressure) only the changes in lattice constant were considered in the calculation of the potential. As far as pressure is concerned this approach is justified and, indeed, our fit of the  $p$ -dependent phonon frequencies is better than that obtained in the case of the  $T$  dependence. Also the fit obtained for  $\Delta(p)$  is reasonably good considering the experimental error in determining  $\Delta(p)$ .

But the temperature dependence seems certainly less rewarding. While the values of  $\Delta$  could be fitted very well, the calculated frequencies depart from the corresponding

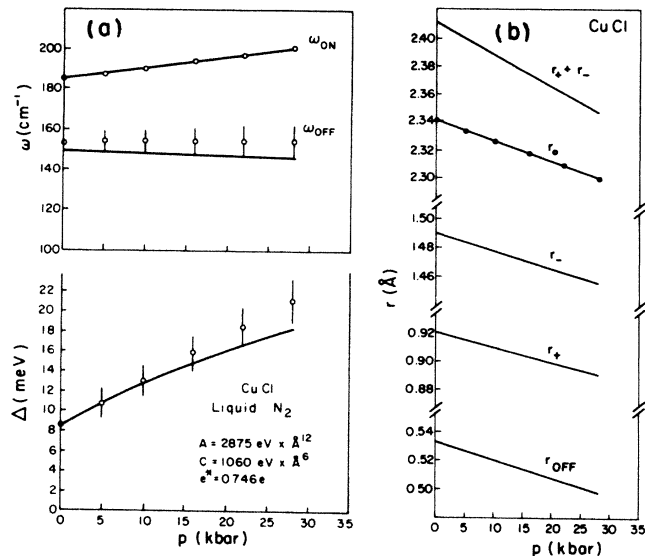


FIG. 8. (a) The pressure dependence of  $\omega_{on}$ ,  $\omega_{off}$ , and  $\Delta$ . Points: experimental [from the spectra of Shand and Hanson (Ref. 22)]. Solid lines: calculated (the parameters are also indicated). (b) The pressure dependence of the ionic radii and their sum as compared to that of  $r_0$ . The calculated off-center position  $r_{off}$  is also plotted versus  $p$ .

experimental values at temperatures higher than 170 K [see Fig. 7(a)]. Besides, attempts to calculate the frequencies at  $T > 300$  K lead to even higher disagreement with the measured values:<sup>51</sup> the calculated  $\omega_{on}$  decreases slower than the experimental one, while the  $\omega_{off}$  we obtain even increases. One should have expected this from a calculation which relies solely on the thermal expansion of the lattice. A change in frequency of  $\Delta\omega_{on} = 10$   $\text{cm}^{-1}$  is obtained experimentally either for  $\Delta p = 22$  kbar or for  $\Delta T = 300$  K, but the change of the lattice constant for  $\Delta p = 22$  kbar is 15 times larger than that induced by  $\Delta T = 300$  K. It is clear that other factors, such as the amplitude of vibration of the ions, should have been taken into account. When temperature is increased,  $\langle u^2 \rangle$  of the cations in CuCl increases drastically,<sup>27</sup> a fact which makes our approximation of “small vibrations around the equilibrium point” poor at high temperatures.

As a result of our calculations we also obtain  $r_{off}(T)$  and  $r_{off}(p)$ , which are of the order of 0.5 Å [see Fig. 7(b) and 8(b)]. This brings up two questions which we are going to discuss: (i) Is the order of magnitude of  $r_{off}$  reasonable when compared with structural measurements? (ii) Is its temperature and pressure dependence in agreement with those found by structural study?

(i) In the original “disorder model” proposed by Sakata *et al.*<sup>25</sup> they obtained much smaller displacements:  $r_{off} \approx 0.13$  Å, which are also very small when compared to off-center positions of  $\text{Cu}^+$  impurities in different alkali halides. In their recent EXAFS work, Boyce *et al.*<sup>1</sup> obtained for room temperature the value of  $r_{excluded} = 2.24$  Å, while the minimum anion-cation distance obtained in our calculations is  $r_1 = 2.22$  Å, which corresponds to  $z = r_{off} = 0.5$  Å. In this sense the volume which is allowed for the  $\text{Cu}^+$  ion in the  $\text{Cl}^-$  cage by the EXAFS model is

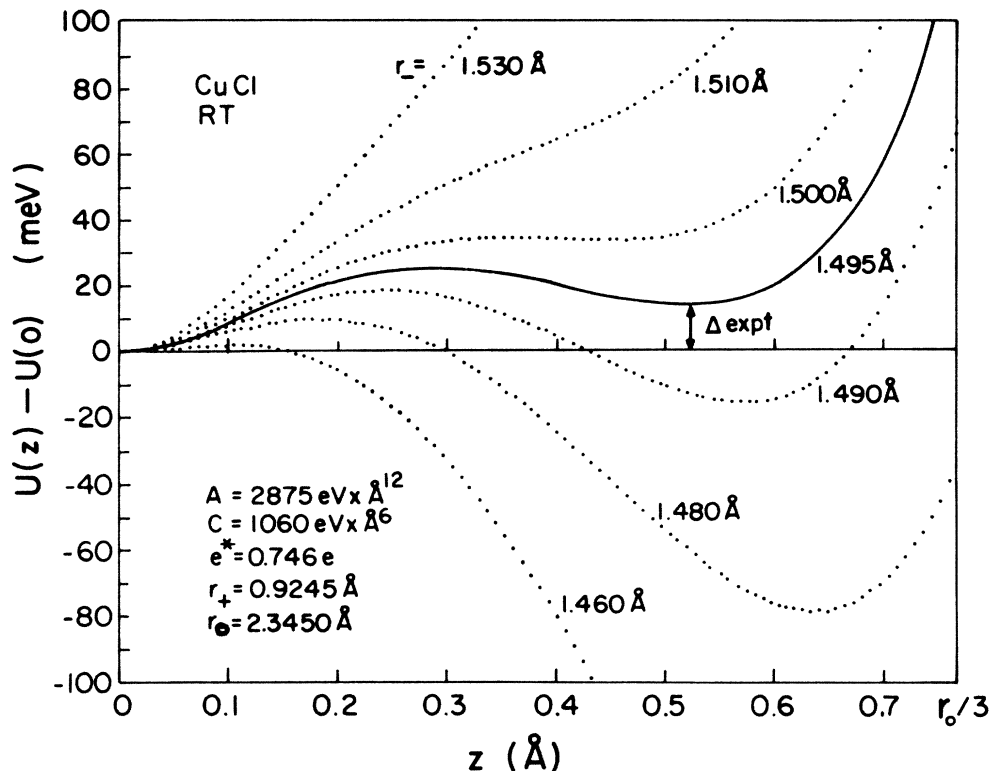


FIG. 9. The different shapes of  $U(z)$  when  $r_-$  is changed while the other parameters are kept constant. Solid line: the fit to the measured  $\omega_{on}$ ,  $\omega_{off}$ , and  $\Delta$ .

comparable with a displacement of 0.5 Å from the central position.

Also the contour plots of the Cu ion density in the (110) plane (Fig. 12a in Ref. 1) are very similar to the "tunneling orbits" we have described in our Fig. 4(b).

For lower temperatures, EXAFS data are available at 77 K only. These data served as a structural standard, used to determine the unknown Cu-Cl pair correlation function at elevated temperatures.<sup>1</sup> The authors fit their results at 77 K using a narrow Gaussian with four halogen nearest neighbors centered at  $r_0 = 2.34$  Å. The width is estimated to be 0.06 Å, which is in disagreement with our results at 77 K: for our  $r_{off}$  of about 0.53 Å the Cu-Cl distances can be as small as 2.24 Å and as large as 2.87 Å. In our model the distribution of the Cu ions is described by a superposition of three narrow Gaussians, centered at distances  $r_1$ ,  $r_0$ , and  $r_0 + r_{off}$ . The off-center model assumes that the Cu ion spends considerably more time in the central well than in each of the four off-center wells. Therefore the Cu-Cl distribution would appear as having a strong and sharp peak at  $r_0$  and two secondary peaks, much lower, corresponding to the off-center positions. But this distribution would show a beating pattern in the single-shell EXAFS spectrum<sup>28</sup> due to interference between contributions from Cu atoms at the three radial distances from a Cl atom. Such beatings have *not* been noticed.<sup>1,28</sup> Moreover, attempts to fit EXAFS data in CuBr using the off-center model<sup>28</sup> have failed. It should, however, be noted again that EXAFS results at tempera-

tures  $T > 80$  K could not be analyzed in the harmonic approximation neither in CuCl nor in CuBr: models as the "excluded volume"<sup>1</sup> or an anharmonic single particle potential<sup>28</sup> for the Cu ion had to be used. Hence, there is no structural evidence for off-center Cu ions in CuCl or in CuBr, though there is plenty of evidence that the harmonic approximation fails.

(ii) The function  $r_{off}(p)$  is quite similar to  $r_0(p)$  [see Fig. 8(b)] which may easily be understood. The effect of temperature is strikingly different:  $r_{off}$  decreases strongly with temperature up to 170 K, while the lattice constant barely changes [see Fig. 7(b)]. This may be related to the high vibrational amplitudes of  $\text{Cu}^+$  which grow with temperature faster than  $r_0$  does. Eventually  $r_{off}$  levels off in the temperature range  $170 < T < 300$  K. When extrapolating the calculation to temperatures higher than 300 K one obtains an increase in  $r_{off}$ , which will produce a decrease in the  $r_1$  distances, in agreement with the decrease of  $r_{excluded}$  obtained in EXAFS.<sup>1</sup> Such high values for  $r_{off}$  would imply very large width of the off-center wells—seemingly larger than the one we already allowed for. A larger width would also decrease the curvature around the minimum, decreasing the calculated frequencies, which would improve the fit to the measured ones at these temperatures.

We shall now discuss the values which we obtained for the parameters  $A$ ,  $C$ ,  $r_+$ , and  $r_-$ , including our values at room temperature and normal pressure. The values we obtain for  $r_+$  and  $r_-$  are smaller than the "free ionic ra-

dii"; while the cation radius is only 4% smaller, the anion is 20% smaller than the free ion. The only crystalline radius we came across has been reported by Huggins and Mayer<sup>52</sup> for Cl<sup>-</sup> and agrees with our value. The additivity rule still fails:

$$r_+ + r_- = 0.92 \text{ \AA} + 1.49 \text{ \AA} = 2.41 \text{ \AA} > 2.34 \text{ \AA},$$

which means that the ions still overlap.

The other two constants are  $A$  and  $C$ . In Table IV we have included the existing information about them, as well as the values we have used. When calculating the vdW constant after Bucher we have used the London formula:<sup>42</sup>

$$C = \frac{2}{3} \frac{R_+^{(2)} + R_-^{(2)}}{E_+ + E_-}. \quad (5.11)$$

Here  $R_+^{(2)}$  and  $R_-^{(2)}$  are the second orbital moments of the ions,  $E_+$  and  $E_-$  are approximately equal to their ionization potentials. Using Bucher's quantum mechanical calculation for the second orbital moments we obtained the result followed by  $R^{(2)}$  in brackets in Table IV. Since the values obtained in Bucher's calculation for the first-order orbital moment  $\langle r \rangle$  were lower than the actual ionic radii (see Table V) we have calculated the ratios:

$$s_+ = r_+ / \langle r_+ \rangle \quad \text{and} \quad s_- = r_- / \langle r_- \rangle.$$

If one simply multiplies the calculated  $R^{(2)}$  values by this ratio squared ( $s^2 R^{(2)}$ ) one obtains for the vdW constant a value very close to that used by us.

For the repulsion constant  $A$ , the value we have obtained is about 2 times smaller than the reported values. This is the direct result of the strong constraint we have imposed on the potential: to have more than one minimum. But one should bear in mind that the values reported for the Born-Mayer constants are model dependent.

## VI. SUMMARY AND CONCLUSIONS

We have presented here an actualized review of the experimental anomalies in the optical-phonon spectrum of CuCl, relating them to similar features observed in CuBr, CuI, AgI, as well as in the mixed Cu halides and in  $\text{Cu}_x\text{Ag}_{1-x}\text{I}$ . As far as CuCl is concerned we have concluded that its  $\mathbf{k}=0$  optical-phonon spectrum contains *two* polar modes,  $\beta$  and  $\gamma$ , which are strongly affected by temperature and pressure. We have shown that the off-center model is able to explain qualitatively all the peculiarities observed in the pure crystals, as well as some of the results in the mixed crystals. We have then proposed a theoretical expression for the cation potential in CuCl, which enabled us to make quantitative predictions in the frame of the off-center model. The following assump-

TABLE V. The ionic radii of Cu<sup>+</sup> and Cl<sup>-</sup>.

|          | Tables free | Bucher <sup>a</sup> $\langle r \rangle$ | Huggins <sup>b</sup> in crystal | This work CuCl |
|----------|-------------|---|---------------------------------|----------------|
| $r_+(A)$ | 0.96        | 0.52                                    |                                 | 0.92           |
| $r_-(A)$ | 1.81        | 1.09                                    | 1.48                            | 1.49           |

<sup>a</sup>Reference 44.

<sup>b</sup>Reference 52.

tions were used in building up this potential (a) The CuCl crystal is an ensemble of identical and independent Cu<sup>+</sup>(Cl<sup>-</sup>)<sub>4</sub> tetrahedra. (b) The potential includes the Madelung term and two short-range interactions: the van der Waals attraction with distance-dependent polarizabilities for both the anion and the cation, and the Born-Mayer-Verwey repulsion. The parameters of the potential are the ionic radii and the vdW and BMV interaction constants.

We have expressed the potential of the cation in terms of  $z$ , its displacement from the ideal site along the [111] direction. The parameters were chosen such as to lead to a potential with *two* minima, with an energetic difference between them equal to the experimental  $\Delta$  and with second derivatives in each minimum yielding the measured on and off optical-phonon frequencies. Using reasonable values for the parameters we have obtained the correct shape of the potential. The position of the off-center  $r_{\text{off}}$  has also been obtained from the calculations. It was found to be at distance of about 0.5 Å from the ideal lattice site, and it is temperature and pressure dependent. In spite of the rough approximation we have used, the fit to the experimental values of the temperature- and pressure-dependent phonon frequencies and  $\Delta$ 's is remarkable.

*Note added in proof.* Since the original submission of this manuscript, G. Kanellis *et al.* showed<sup>53,54</sup> that a Fermi resonance of TO( $\gamma$ ) with the two-phonon density of states they calculated gives the line shapes of TO( $\gamma$ ) in the three Cu halides. These authors do not address the other anomalies in the optical-phonon spectra of the pure and mixed Cu halides reviewed in the present paper, such as the disorder-induced lines in the Raman spectra of both the pure and mixed crystals.

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