Analysis of the off-center effect of Cu$^+$ in alkali halides using crystal-field theory

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We have found that the relative intensity of the $^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ crystal-field components of the $3d^{10} \rightarrow 3d^9 4s$ transition of Cu$^+$ in alkali halide hosts provides a measure of the Cu$^+$ ground-state off-center displacement along the [111] axis. This is shown by deriving the crystal-field potential that describes the off-center effect of Cu$^+$, and then calculating the transition moments to the ^1E_g and $^1T_{2g}$ final states. By analyzing the spectra of Cu$^+$ in numerous alkali halide hosts, it is found that the degree of off-center displacement increases with the lattice constant of the alkali halide.

I. INTRODUCTION

The spectra of transition-metal-ion impurities have long been understood on the basis of crystal-field theory. Here, the impurity is assumed to be surrounded by negative point charges, and the splitting of the d orbitals are calculated by considering the electrostatic multipole contributions from the environment. Crystal-field theory is known, however, not always to reproduce the spectra quantitatively, although it has been successful at indicating the important physical mechanisms and predicting trends. In this work, we use crystal-field theory to calculate the odd-parity multipole contributes to the potential that result from the displacement of the Cu$^+$ ion off the center of the metal site in alkali halide crystals. We then use this information to calculate the relative transition strength of two crystal-field-split bands of Cu$^+$. We find that this relative transition intensity is sensitive to the magnitude of the impurity off-center displacement and therefore can be used to give detailed information about the ground-state position of Cu$^+$ in the alkali halide hosts.

The spectral properties of Cu$^+$-doped alkali halide crystals have been studied for several decades, one result being that the near-uv absorption bands due to the spin-allowed $3d^{10} \rightarrow 3d^9 4s$ transitions of Cu$^+$ have now been extensively documented. Several absorption bands are typically observed, in part due to the octahedral-crystal-field splitting of the $3d^9 4s$ excited state into E_g- and T_{2g}-type components. These assignments have only recently become definitive due to the experiments of McClure and co-workers, in which two-photon spectroscopy was used to identify the $^1A_{1g}(3d^{10}) \rightarrow {}^1E_g(3d^9 4s)$ and the $^1A_{1g}(3d^{10}) \rightarrow {}^1T_{2g}(3d^9 4s)$ transitions for several Cu$^+$-doped alkali halides.[1-6]

The above picture is based on the assumption that when the Cu$^+$ impurity substitutionally replaces the host cation, it remains at the center of the octahedron of halide ions. Since the $d \rightarrow s$ transition is one-photon parity forbidden, the average value of the displacement of Cu$^+$ from the center of the octahedron, be it thermally activated or a static effect, determines whether the transition is allowed. Although ground-state Cu$^+$ is, on the

average, on center in LiCl, NaF, NaCl, and KF, the most stable position of Cu$^+$ is known to be located off center along the [111] axis in other crystals such as KCl, RbCl, NaBr, KBr, RbBr, and NaI.[1,2,6-10] As a result of this distortion, Cu$^+$ moves closer to three halides ions and further from the other three, lowering the site symmetry from O_h to C_{3v} and destroying the inversion symmetry. Although the off-center displacement is known to mix the $^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions with each other and with other transitions, the centrosymmetric model is a useful starting point from which to describe the system.[4]

To provide an example of the spectra of typical on-center and off-center systems, the excitation spectra for Cu$^+$-doped NaCl and KCl, respectively, are reproduced in Fig. 1 from the work of Nagasaka et al.[11] (The excitation spectra of Cu$^+$-doped alkali halides, as obtained by monitoring the $^3E_g \rightarrow {}^1A_{1g}$ emission, are generally quite similar to the absorption data, although they are not beset by scattering background interferences, and are therefore often easier to examine). The $^1A_{1g} \rightarrow {}^1E_g$ and $^1T_{2g}$ transitions have been previously identified for these systems using two-photon excitation spectroscopy;[4] these assignments are indicated in the figure. It is clear that the relative intensity of these two transitions is reversed in the NaCl and KCl systems. It is the purpose of this work to show that the reversal of the relative intensity of the $^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions is a direct consequence of the stable ground-state position of Cu$^+$ shifting from being on center to off center.

Previous workers have successfully related the oscillator strength of the $d \rightarrow s$ transition to the ground-state position of Cu$^+$.[8,10] The off-center systems have oscillator strengths on the order of 0.05, and due to the static nature of the distortion, the f number is nearly independent of temperature. On the other hand, the on-center Cu$^+$ systems have smaller oscillator strengths of about 0.001 at low temperature, and tend to increase by a factor of 2–5 at higher temperatures. The present work is essentially an extension of this effort to relate the spectral properties of the $d \rightarrow s$ transition to the ground-state position. We use the standard methods of crystal-field theory to show that the *relative* intensity of the
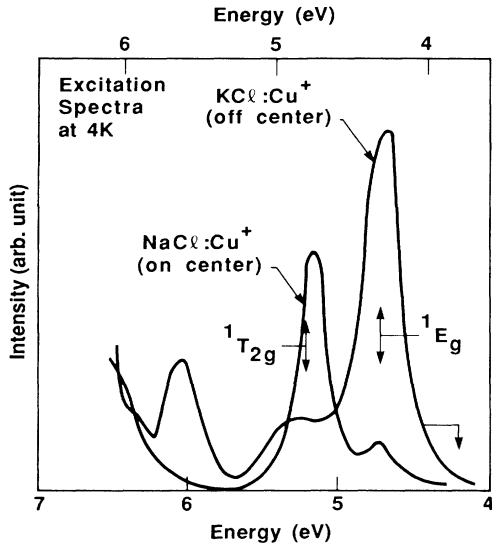
Energy (eV)

FIG. 1. Excitation spectra of typical on-center ($NaCl:Cu^+$) and off-center ($KCl:Cu^+$) systems, data taken from Nagasaka et al. (Ref. 11); obtained by monitoring the $^3E_g \rightarrow {}^1A_{1g}$ luminescence. Note that the relative strength of the $^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions is reversed for $NaCl:Cu^+$ and $KCl:Cu^+$. The $KCl:Cu^+$ and $NaCl:Cu^+$ spectra are referred to the lower and upper energy scales, respectively.

$^1A_{1g} \rightarrow {}^1E_g$ and the $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions is an accurate signature of the magnitude of the off-center displacement. The profusion of data available for Cu^+ systems and the inherent simplicity of the $d \rightarrow s$ transition provide a unique opportunity to understand this interconfigurational transition in great detail.

This paper is arranged as follows. In Sec. II the theory of the relative transition strength of the crystal-field components is calculated assuming that the angular quantum numbers of the $3d$ and $4s$ orbitals remain good quantum numbers. In Sec. III the $^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions are identified in as many alkali halide hosts as possible, and in Sec. IV the ratio of these transition strengths is found to be a smoothly varying function of the lattice constant of the host. The possible physical basis for this remarkable dependence is considered. Finally, Sec. V contains a summary of the conclusions.

II. THEORY

A. General considerations

In this section we will develop the necessary equations to calculate the relative rate of the $^1A_{1g}(d^{10}) \rightarrow {}^1E_g(d^9s)$ and $^1A_{1g}(d^{10}) \rightarrow {}^1T_{2g}(d^9s)$ transitions of Cu^+. The transition rate from state G to state F can, in general, be written as[12]

$$R = \frac{2\pi}{\hbar^2} |\langle G | \mu | F \rangle|^2 g(\nu) , \tag{1}$$

where μ is the dipole-moment operator and $g(\nu)$ is the line-shape function. Consider a system where the Hamiltonian can be written as

$$H = H_0 + \Delta V , \tag{2}$$

where ΔV is a small perturbation. If $|G\rangle$ and $|F\rangle$ are eigenfunctions of H_0 and the $G \rightarrow F$ transition is forbidden in zeroth order, we can write that

$$\langle G | \mu | F \rangle = 0 . \tag{3}$$

The transition moment may nevertheless be nonzero due to the effect of ΔV if the moment from first-order perturbation theory is found to be nonzero, i.e.,

$$\sum_I \left[\frac{\langle G | \Delta V | I \rangle \langle I | \mu | F \rangle}{E_I - E_G} \right. $$
$$\left. + \frac{\langle G | \mu | I \rangle \langle I | \Delta V | F \rangle}{E_I - E_F} \right] \neq 0 , \tag{4}$$

where the summation is over all states of the system. If we take the energy difference in the denominator as a constant, we can apply the closure approximation to Eq. (4).[13] The transition rate is then expected to be proportional to a matrix element of the form

$$|\langle G | \Delta V \mu + \mu \Delta V | F \rangle|^2 .$$

Recognizing that, for the case of Cu^+, $G = {}^1A_{1g}(d^{10})$ and $F = {}^1E_g(d^9s)$ or $^1T_{2g}(d^9s)$, we can describe the transition as the result of promoting an electron from a linear combination of d orbitals to an s orbital. Also, if the radiation field is assumed to be polarized along the z axis, we can take $\mu = erY_{10}$, where Y_{LM} is a spherical harmonic of rank L, e is the electron charge, and r is the electronic radial coordinate. Therefore, to within a constant, the rate R_α can be described with

$$R_\alpha = \left| \sum_m a_m^\alpha \langle 2m | \Delta VrY_{10} + rY_{10}\Delta V | 00 \rangle \right|^2 , \tag{5}$$

where α denotes either the $^1A_{1g} \rightarrow {}^1E_g$ or the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition as E or T, respectively, and the a_m^α are the appropriate linear combinations of d orbitals that have been split by the cubic component of the octahedral field. For the ^1E_g state the d orbitals are written as[14]

$$|e_g\theta\rangle = |20\rangle, \quad |e_g\epsilon\rangle = \frac{1}{\sqrt{2}}(|22\rangle + |2-2\rangle) , \tag{6a}$$

while for the $^1T_{2g}$ state they are

$$|t_{2g}1\rangle = |2-1\rangle, \quad |t_{2g}0\rangle = \frac{1}{\sqrt{2}}(|22\rangle - |2-2\rangle) ,$$
$$|t_{2g}-1\rangle = -|21\rangle . \tag{6b}$$

The nature of the perturbation ΔV will be considered below for the cases of the vibronically induced intensity of on-center Cu^+, and for the static perturbation experienced by off-center Cu^+.

B. Form of ΔV

We now need to derive the analytical expression for ΔV. The negative Coulombic potential field experienced by an ion in a crystal can, in general, be written as[14]

$$V = \sum_{L=0}^{\infty} \sum_{M} r^L \gamma_{LM} Y_{LM}(\theta,\phi) , \tag{7a}$$

where

$$\gamma_{LM} = \frac{4\pi e}{2L+1} \int \frac{\rho(R) Y_{LM}(\Theta,\Phi)}{R^{L+1}} d\tau . \tag{7b}$$

In Eqs. (7), (r,θ,ϕ) denotes the field point coordinate while (R,Θ,Φ) is that of the negative source charge density of the neighboring anions.

The function $\rho(R)$ describes the radial charge distribution surrounding the Cu$^+$ ion. For group-theoretical reasons, only the spherical harmonics of rank $L=1$ and 3 can induce oscillator strength into the $3d \to 4s$ or $l=2 \to l=0$ transition of Eq. (5). If the six halide ions were arranged around the Cu$^+$ ion such that they were point charges at the vertices of a regular octahedron, the $L=1$ and $L=3$ components of the potential would be identically equal to zero. We can, however, model the effects of the off-center displacement of Cu$^+$ by shifting three of the halides from R to $R+\Delta R$, and moving the other three to $R-\Delta R$, as shown in Fig. 2. With this model for the off-center displacement of Cu$^+$ we find the perturbed potential to be

$$\Delta V = \Delta V_{L=1} + \Delta V_{L=3} , \tag{8a}$$

where

$$\Delta V_{L=1} = \left[\frac{4\pi}{3} \right]^{1/2} e \left[\frac{1}{(R+\Delta R)^2} - \frac{1}{(R-\Delta R)^2} \right] r$$

$$\times \left[\frac{-1}{\sqrt{2}} [(1+i)Y_{11} - (1-i)Y_{1-1}] + Y_{10} \right] \tag{8b}$$

and

$$\Delta V_{L=3} = \left[\frac{\pi}{28} \right]^{1/2} e \left[\frac{1}{(R+\Delta R)^4} - \frac{1}{(R-\Delta R)^4} \right] r^3$$

$$\times \{ -\sqrt{5}[(1-i)Y_{33} + (1+i)Y_{3-3}]$$

$$+ \sqrt{3}[(1+i)Y_{31} - (1-i)Y_{3-1}] + 4Y_{30} \} . \tag{8c}$$

C. Calculation of transition rates

Now, we need to couple Eqs. (8b) and (8c) with the photon field and determine the resulting $L=2$ components as required by Eq. (5). We find that[15]

$$(\Delta V_{L=1} r Y_{10} + r Y_{10} \Delta V_{L=1})_{L=2} = (\tfrac{16}{15})^{1/2} e \left[\frac{1}{(R+\Delta R)^2} - \frac{1}{(R-\Delta R)^2} \right] r^2 \{ -(\tfrac{3}{8})^{1/2}[(1+i)Y_{21} - (1-i)Y_{2-1}] + Y_{20} \} \tag{9a}$$

and

$$(\Delta V_{L=3} r Y_{10} + r Y_{10} \Delta V_{L=3})_{L=2} = \tfrac{6}{7}(\tfrac{3}{5})^{1/2} e \left[\frac{1}{(R+\Delta R)^4} - \frac{1}{(R-\Delta R)^4} \right] r^4 \left[\frac{1}{\sqrt{6}} [(1+i)Y_{21} - (1-i)Y_{2-1}] + Y_{20} \right] . \tag{9b}$$

By substituting into Eqs. (5) and (6), and simplifying the expression as much as possible, we find that the ratio of the rates (or strengths) of the $^1A_{1g} \to {}^1E_g$ and $^1A_{1g} \to {}^1T_{2g}$ transitions, R_E and R_T, is

$$\frac{R_E}{R_T} = \left| \frac{\sqrt{2} + \sqrt{3}\beta(1+3\Delta^2)}{\sqrt{3} - \sqrt{2}\beta(1+3\Delta^2)} \right|^2 , \tag{10a}$$

where $\Delta = \Delta R / R$ is the fractional displacement of the halide ions, and

$$\beta = \frac{6}{7} \left[\frac{3}{2} \right]^{1/2} \frac{\langle 3d \mid r^4 \mid 4s \rangle}{R^2 \langle 3d \mid r^2 \mid 4s \rangle} \tag{10b}$$

is a measure of the importance of the $\Delta V_{L=3}$ term relative to the $\Delta V_{L=1}$ term. In Fig. 3 the value of R_E/R_T is plotted against the fractional displacement for several possible values of β. We assume β is positive since the electron integrals probably have the same sign. Although Eqs. (10) are a fairly crude result since it assumes that the anions can be described as point charges, it does clearly show that a larger displacement implies a greater value of R_E/R_T. For the case where Cu$^+$ is nearly on center and β is small, the R_E/R_T ratio reduces to 0.67, the degeneracy-weighted ratio. As the displacement of the Cu$^+$ ion increases, the $\beta\Delta^2$ terms will add to the numerator and subtract from the denominator, increasing the value of R_E/R_T. In other words we can expect that the relative intensity of the $^1A_{1g} \to {}^1E_g$ and $^1A_{1g} \to {}^1T_{2g}$ transitions will essentially provide a measure of the off-center displacement of Cu$^+$.

D. Physical understanding of Eq. (10)

We now consider our model in simple physical terms. The field due to the $\Delta V_{L=1}$ term perturbs the e_g and t_{2g}
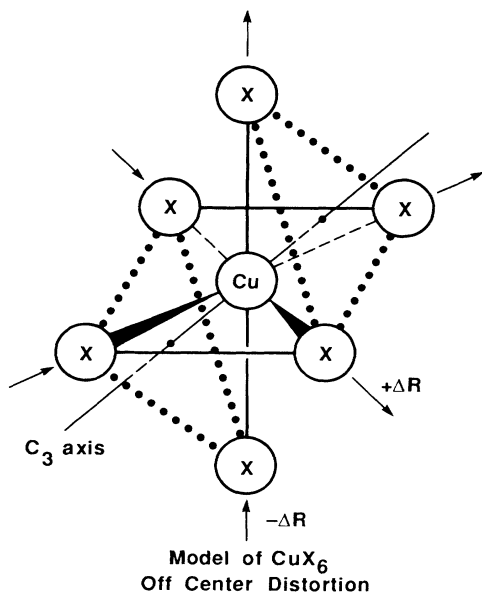
Model of CuX$_6$
Off Center Distortion

FIG. 2. Model of the Cu$^+$ off-center distortion used to calculate the crystal-field potential in Eq. (8). Three halide ions move ΔR away from the central Cu$^+$ ion; the three other halides move ΔR inward.
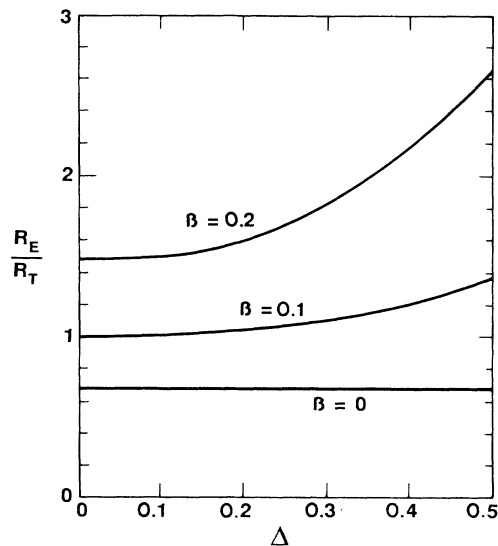

FIG. 3. Plot of the calculated relative intensity of the $^1A_{1g} \rightarrow {^1E_g}$ and $^1A_{1g} \rightarrow {^1T_{2g}}$ transitions of Cu$^+$, R_E/R_T, as a function of the fractional displacement of the halide ions used to model the off-center effect Δ; see Fig. 2 and Eq. (10). These calculations show that larger values of R_E/R_T imply greater off-center displacement.

orbitals equivalently and therefore gives the degeneracy-weighted transition strength ratio, 2/3. The $\Delta V_{L=3}$ term, on the other hand, reflects the corrugation of the equipotential surface caused by the six negative charges of the octahedron. In effect, the octahedral field causes the potential to change more steeply along the [100] direction compared to $\Delta V_{L=1}$ and less so along the [110] axis. Since the e_g and t_{2g} orbitals point along the [100] and [110] directions, respectively, the $\Delta V_{L=3}$ potential increases the strength of the $e_g \rightarrow s$ transition, and decreases that of the $t_{2g} \rightarrow s$ transition.

Although Eq. (10) provides us with a good understanding of the physical mechanism involved, we must recognize the limited quantitative utility of this relationship. When the displacements become large, many more effects are likely to become important. A few examples are higher-order terms in the potential, and the mixing of the ^1E_g and $^1T_{2g}$ states by the crystal field. In addition, the exact nature of the nuclear displacements of the nearest neighbors of the Cu$^+$ site is at present unknown. Finally, the neglect of the covalent interactions with the halides may be quite significant.

It is satisfying to note that Eq. (10) is also in agreement with the qualitative predictions of molecular-orbital (MO) theory. This agreement is analogous to the MO and crystal-field descriptions of the octahedral-field splitting of the e_g and t_{2g} d orbitals.[13] Roughly speaking, crystal-field theory indicates that since the e_g orbitals point at the negatively charged ligands, they have a higher energy than that of the t_{2g} orbitals, which are directed between the charges. In the language of MO theory, the e_g orbitals have a strong σ antibonding interaction with the p orbitals of the halide ions and are significantly raised in energy, while the t_{2g} orbitals ex-

perience only weak π bonding that is approximately nonbonding in nature. These same principles apply to the understanding of the transition moments induced by the off-center effect. As Cu$^+$ is displaced off the center of the octahedron, the e_g orbitals will strongly mix via σ bonding with the odd-parity MO's composed of the halogen p orbitals, while the t_{2g} orbitals will remain mostly nonbonding. These odd-parity MO's will serve to induce oscillator strength into the $e_g \rightarrow s$ transition. These bonding considerations are related to the theory of Nagasaka, who has considered the mixing of charge-transfer transitions into the $d \rightarrow s$ transitions.[8,16]

III. ANALYSIS OF THE ABSORPTION SPECTRA

According to the theoretical developments in Sec. II, the relative absorption band strength of the $^1A_{1g} \rightarrow {^1E_g}$ and the $^1A_{1g} \rightarrow {^1T_{2g}}$ transitions should be approximately $R_E/R_T = 0.67$ for the on-center Cu$^+$, and > 0.67 for the off-center case. Equation (10) predicts that a greater off-center displacement implies a greater R_E/R_T ratio. We now consider the actual absorption spectra of numerous Cu$^+$-doped alkali halides to see if these predictions are, in fact, borne out.

As previously discussed, two-photon spectroscopy has been used to assign the $^1A_{1g} \rightarrow {^1E_g}$ and $^1A_{1g} \rightarrow {^1T_{2g}}$ transitions of Cu$^+$ in the hosts NaF, LiCl, NaCl, and KCl,[2,4] while one-photon absorption or excitation spectra exist for almost all Cu$^+$-doped alkali halides. Fortunately, the optical spectra of these materials are sufficiently similar that these two transitions can be identified by analogy for most of the other alkali halides. The results of these assignments are in Table I, where

TABLE I. Optical properties of Cu$^+$ in alkali halide crystals. (Question marks indicate that results were not available.)

Crystal	Nearest-neighbor distance (Å)	$d \rightarrow s$ absorption peaks (eV)		R_E/R_T	Ground-state-position
		$^1A_{1g} \rightarrow {}^1E_g$	$^1A_{1g} \rightarrow {}^1T_{2g}$		
LiF	2.014	?	?	?	?
NaF[a]	2.317	4.15	4.49	0.52	Harmonically on center
KF[b]	2.674	4.37	4.82	0.55	On center
RbF	2.815	?	?	?	?
LiCl[c]	2.570	4.88	5.41	0.52	Harmonically on center
NaCl[d]	2.820	4.44	4.79	0.22	Anharmonically on center
KCl[e]	3.147	4.75	5.30	5.1	Deep off center
RbCl[f]	3.291	4.70	5.29	7.6	Off center
LiBr	2.751	?	?	?	?
NaBr[g]	2.989	4.69	5.12	1.5	Shallow off center
KBr[h]	3.298	4.66	5.27	6.0	Deep off center
RbBr[i]	3.445	4.61	4.94	4.7	Off center
LiI[j]	3.000	4.97	5.20	1.2	?
NaI[k]	3.237	4.75	?	?	Deep off center
KI[l]	3.533	4.73	?	?	Deep off center
RbI[j]	3.671	4.64	4.93	7.2	Off center

[a]References 1 and 2.
[b]References 6 and 7.
[c]References 7, 8, 17, and 18.
[d]References 8, 10, and 19–21.
[e]References 8, 10, 11, and 22.
[f]References 8 and 9.

[g]References 9, 10, and 23–25.
[h]References 22 and 26.
[i]Reference 9.
[j]References 27 and 28.
[k]References 10, 27, and 28.
[l]References 22, 27, and 28.

the $d \rightarrow s$ absorption peak energies and the R_E/R_T ratios have been tabulated.[1,2,6–11,17–28] We have actually used the absorption band heights to calculate the values of R_E/R_T in Table I, since the height is expected to be approximately proportional to the band area. The height of each band was determined by critically comparing the ratios obtained from various absorption and excitation spectra that are available in the literature for each Cu$^+$-doped system. When necessary, a background was subtracted from the absorption data. The Jahn-Teller splitting of the ^1E_g state was ignored in this analysis.[2] Further analysis of the spectra bands, (such as calculating the band area instead of only its height), is not warranted in light of the observed variation of the spectra reported in the literature and of the uncertainties of the base lines that needed to be subtracted from many of the absorption spectra. As we shall see, however, the simple spectral analysis utilized reveals quite satisfactorily the change in the relative Cu$^+$ band strengths among the alkali halide hosts.

In the last column of Table I, the stable ground-state position of Cu$^+$ is indicated. This information has been derived from several types of experimental evidence. The Cu$^+$ ion in NaF, KF, LiCl, and NaCl has been recognized as being on center by noting the significant increase of the oscillator strength of the $d \rightarrow s$ transition when the crystal is warmed from 4 K to room temperature. On the other hand, the oscillator strengths of the off-center systems have been found to be nearly temperature independent. Other kinds of measurements involving ionic thermocurrents[22] and the dielectric response[10] of the crystals have confirmed and quantified the off-center displacement of Cu$^+$ in such crystals as KCl,

NaI, KBr, and KI. These experiments have yielded displacements on the order of 1 Å, showing that the values of 0.5Δ plotted in Fig. 3 are within reason. By examining the data in Table I, we see that the value of R_E/R_T is clearly correlated with the extent of the off-center displacement. The on-center systems have $R_E/R_T = 0.2–0.5$ while the deep off-center systems give 5–7. Furthermore, the sensitivity of the absorption spectra of NaBr:Cu$^+$ to applied pressure has been interpreted to mean that NaBr:Cu$^+$ is a "shallow" off-center system,[10] and, in agreement, its R_E/R_T ratio is intermediate between those of the on- and off-center systems. Thus the information in Table I gives evidence that the value of R_E/R_T is a measure of the extent of the off-center displacement of Cu$^+$.

IV. DISCUSSION

The identity of both the cation and the anion of the alkali halide crystal affects whether Cu$^+$ is on or off center. The understanding of the cation is rather straightforward and will be considered first. It has been previously recognized that Cu$^+$ will be off center if it replaces an alkali ion of greater ionic radius, while it will be squeezed on center if the alkali-ion radius is less.[22] The trend exhibited by LiCl, NaCl, and KCl supports this criterion. The Li$^+$ ion, being much smaller than Cu$^+$, results in a harmonically on-center system with an off-center vibrational frequency of 100 cm^{-1}.[7] Na$^+$ and Cu$^+$ have nearly the same ionic radius, and, in agreement, NaCl:Cu$^+$ has been found to be an anharmonically on-center system.[8] The off-center vibrational frequency is only 23 cm^{-1},[29] showing that the central position is

substantially less stable compared to LiCl:Cu$^+$. Finally, the KCl:Cu$^+$ is known to be a "deep" off-center system.

To illustrate the effect of the anion, let us consider the NaF, NaCl, NaBr, and NaI series. Cu$^+$ is known to be harmonically on center in NaF with an off-center vibrational frequency of 200 cm^{-1}.[4] As mentioned, the off-center frequency of NaCl:Cu$^+$ is much less, being 23 cm^{-1}.[29] Now NaBr:Cu$^+$ has been characterized as a shallow off-center system, while the large, temperature-insensitive oscillator strength of the $d \rightarrow s$ band of NaI:Cu$^+$ indicates that Cu$^+$ is deep off center in this case.[10] So, Cu$^+$ tends to larger off center displacement as we proceed from F$^-$ to I$^-$ and keep the metal ion constant.

It is clear that the tendency for Cu$^+$ to be off center increases with the size of both the cation and the anion.[10] For this reason, the nearest-neighbor (NN) distance of the alkali halide might provide a good overall measure of the off-center displacement expected for Cu$^+$. In fact, if we plot the logarithm of R_E / R_T against the NN distance of the particular alkali halides we find that the points fall on a reasonably smooth curve, as shown in Fig. 4. The average of the experimental R_E / R_T values for the on-center systems, NaF, LiCl, KF, and NaCl, is 0.45, close to the predicted value of 0.67 from Eq. (10). LiI and NaBr appear to be shallow off-center systems, while KCl, RbCl, KBr, RbBr, and RbI are interpreted to be deep off-center crystals.

The data of Fig. 4 shows that the NN distance does provide a useful combined measure of several host properties related to the off-center displacement of Cu$^+$. While the ionic-radius criterion of the cation, discussed above in connection with the LiCl-NaCl-KCl series is
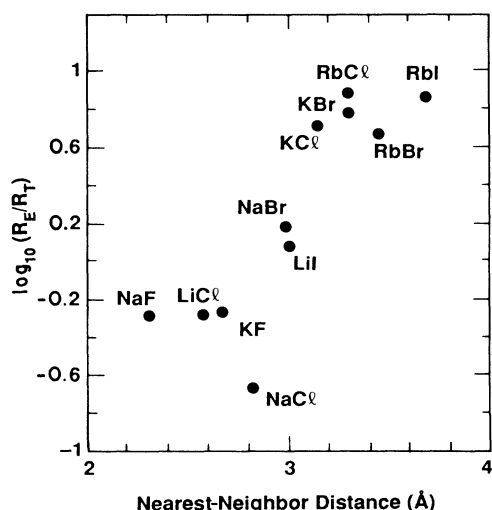

FIG. 4. Plot of the logarithm of the measured relative intensity of the $^1A_{1g} \rightarrow ^1E_g$ and $^1A_{1g} \rightarrow ^1T_{2g}$ transitions of Cu$^+$, log$_{10}(R_E / R_T)$, as a function of the nearest-neighbor cation-anion separation of the particular alkali halide host; see Table I. Since R_E / R_T has been determined to be a measure of the extent of the off-center displacement [see Fig. 3 and Eq. (10)], the data indicates that a greater nearest-neighbor distance results in a larger off-center displacement.

probably valid, the physical origin of the anion dependence is less clear. The position of an impurity ion in a crystal lattice has traditionally been understood to be a function of the electrostatic, repulsive, and polarization energies.[30-33] However, we note that the repulsive and polarization energies are both larger for Cl$^-$ than for F$^-$ at a given impurity–nearest-neighbor separation, and that the relative magnitude of these contributions may be difficult to calculate precisely. In addition, the polarizable nature of Cu$^+$ must be taken into account. Finally, covalent bonding between Cu$^+$ and the halide ions is also likely to play an important role, since it is known from studies of the semiconductors CuCl, CuBr, and CuI that the valence band of these materials results from substantial mixing between the Cu$^+$ $3d$ and the halogen p orbitals.[34]

It is worth mentioning at this point that the main purpose of this work is not to determine the delicate balance of forces that occur at the Cu$^+$ site, but instead to recognize that the relative intensity of the two crystal-field-split $d \rightarrow s$ absorption bands can be used to obtain a measure of the off-center displacement of Cu$^+$. Perhaps future work with the HADES computer code can unravel the exact nature of the lattice relaxation at the Cu$^+$ site.[32]

V. CONCLUSIONS

The Cu$^+$ ion in alkali halide crystals presents a unique opportunity for the investigation of the ground-state off-center effect of an impurity-host system. The simplicity of the physical understanding developed in this work is based on the $d \rightarrow s$, or $l = 2 \rightarrow l = 0$, character of the transition, since, as a result, only operators of rank $L = 2$ can induce oscillator strength into the transition. In addition, since the photon operator transforms as Y_{10}, we only need to consider crystal-field perturbations of rank $L = 1$ and $L = 3$. This work contrasts with the complexity of the $4f \rightarrow 4f$ transitions of trivalent rare-earth ions, where, although mathematical modeling by the Judd-Ofelt theory can be accomplished with only a few parameters, the physical significance of the results is often difficult to establish.[35,36]

There are two basic conclusions in this paper.

(1) The ratio of the oscillator strengths for the $^1A_{1g}(d^{10}) \rightarrow ^1E_g(d^9s)$ and the $^1A_{1g}(d^{10}) \rightarrow ^1T_{2g}(d^9s)$ transitions, R_E / R_T, can be approximately described with

$$\frac{R_E}{R_T} = \left| \frac{\sqrt{2} + \sqrt{3}\delta}{\sqrt{3} - \sqrt{2}\delta} \right|^2 , \tag{11}$$

where the form of δ is obvious by comparison with Eq. (10). For on-center Cu$^+$ systems the δ terms are small and $R_E / R_T = 0.67$, while for statically off-center Cu$^+$ systems the δ terms become important and the transition strength ratio changes such that $R_E / R_T > 0.67$. These predictions were found to be in good agreement with absorption spectra and other independent assessments of the off-center position of Cu$^+$ from the literature as summarized in Table I. The physical mechanism of this reversal of the relative transition strengths with increas-

ing off-center position is attributed to the steeper potential encountered by the e_g orbitals due to the presence of the octahedral electrostatic field, compared to that seen by the t_{2g} orbitals. The quantity R_E/R_T is concluded to be a measure of the off-center displacement of Cu^+.

(2) The off-center displacement of Cu^+ is found to smoothly increase with the nearest-neighbor distance of the alkali halide crystal, as shown in Fig. 4. We are not certain of the physical origin of this effect. This relationship probably exists because the nearest-neighbor distance provides an overall measure of several contributions to the displacement of Cu^+, including the ionic radius of the cation, as well as the bonding and polarizability of the halide ion.

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