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Cu^+ and Ag^+ Centers in Alkali Halides*

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The displacements of Ag^+ and Cu^+ ions in various alkali halides are calculated using a polarizable point-ion model. It is found that Ag^+ in RbCl lies about 0.54 Å along a ⟨111⟩ direction, and that Ag^+ in NaCl, KCl, and RbBr is on site, in agreement with experiment. Cu^+ ions are found to be off center in NaCl, KCl, RbCl, and RbBr, also in ⟨111⟩ directions, by 0.2, 1.36, 1.65, and 1.84 Å, respectively. Using a model of a free Cu^+ ion in a crystalline electric field, the oscillator strength of the $(3d)^{10} \rightarrow (3d)^9 4s$ transition is calculated using Hartree-Fock–Slater wave functions. It is found that the observed oscillator strengths of the order of 0.025 can be induced by fields of 2×10^8 V/cm. This result suggests displacements in the ⟨111⟩ directions about 50% bigger than those given above for the point-lattice model. It turns out also that for Cu^+ in NaCl, oscillator-strength measurements alone are insufficient to decide whether the ion is on site.

I. INTRODUCTION

SINCE the suggestion by Lombardo and Pohl that a Li^+ ion occupies an off-center position in KCl,[1] measurements have been made on certain Ag^+- and Cu^+-doped alkali-halide crystals in an effort to determine in which lattices such impurities would be unstable at normal host cation sites. The normally forbidden $(4d)^{10} \rightarrow (4d)^9 5s$ and $(3d)^{10} \rightarrow (3d)^9 4s$ transitions in these ions become partially allowed either because of the effect of odd lattice vibrational modes or because of a permanent off-center position. At temperatures below 100°K the first effect leads[2,3] to oscillator strengths of the order of 0.001 which vanish at 0°K, the second to an order of magnitude larger oscillator strengths, which are rather temperature-independent. In particular, Dreybrodt and Fussgaenger[4] observed the temperature dependence of the dipole strength of the $(4d)^{10} \rightarrow (4d)^9 5s$ transition of an Ag^+ ion in RbCl. They concluded that the Ag^+ sits in an off-center position in RbCl, and their subsequent calculations indicated that the potential minima were at 0.25 Å from the normal Rb^+ site along a ⟨111⟩ direction. Similar measurements were made on NaCl:Ag and KCl:Ag by Fussgaenger, Martienssen, and Bilz.[5] In these cases, the temperature dependence can be explained by a potential for the Ag^+ having a minimum at the normal lattice site.[4]

Oscillator-strength measurements have also been performed by Gebhardt and Mohler[6] on Ag^+ in KCl using a static electric field along [100], [111], and [110] axes of the crystal and various orientations of the electrical vector of the incicent light. This permitted a detailed analysis of the various states. For an on-site ion, such as Ag^+ in KCl, the field reduces the symmetry of the environment from O_h to C_{4v}, C_{3v}, and C_{2v}, respectively (hence parity is not a good quantum number), and mixes in $4p$ states, thereby changing somewhat the value of the oscillator strength of the vibronically allowed transition. The observed changes in oscillator strength f are of the order 10^{-4}, indicating that here the Ag^+ ion is on site.

Krätzig, Timusk, and Martienssen[7] measured the temperature dependence of the oscillator strength in the range 20–300°K for KCl:Cu, KBr:Cu, and KI:Cu, obtaining 0.025 ± 0.002 for Cu^+ in KCl and 0.056 ± 0.005 for Cu^+ in KBr and KI over the entire temperature range. Their results show that vibronic interactions are not the major cause of the transition and that Cu^+ ions are likely to be off center. If the crystalline electric field is indeed causing the mixing, it is not surprising

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that larger f values are found in the larger KBr and KI lattices in which the Cu^+ ions may go farther off center than in KCl.

In analogy to the studies on KCl:Ag mentioned above, Dultz[8] has investigated the temperature and the applied-electric-field dependence of the oscillator strength of the transitions of Cu^+ in KCl and NaCl. Since here the impurity ion is probably off center, the applied field serves mainly to localize partially the ions along the direction of the field. A large crystalline field at the various off-center positions is then the dominant factor in the mixing of the various states and the oscillator strength can either increase or decrease. Dultz expresses the total oscillator strength f as the sum of the vibronic contribution f_0 and a term proportional to the square of the displacement of the ion from the ideal site x:

$$f=f_0+Ax^2.$$

This follows from the lowest-order term of an expansion of the field in spherical harmonics. His further calculations are based on the somewhat doubtful assumption that the constant A is independent of the host lattice, that is, A is the same for NaCl, KCl, KBr, etc.[9] In this way he obtains for the displacements of Cu^+ in NaCl, KCl, and KBr near 0°K the values 0.0, 0.3, and 0.45 Å along $\langle 111\rangle$, respectively.

Recently, electrocaloric measurements by Kapphan and Lüty[10] confirmed the off-center nature of the Ag^+ ion in RbCl and established a dipole moment of 1.5–2.10 D. No electrocaloric effect was found for Ag^+ in RbBr. Unfortunately, no similar paraelectric cooling experiments have been reported on Cu^+-doped crystals.

Baldini, Jean, and Spinolo[11] have experimentally determined the lifetime of the excited $(3d)^9 4s$ state of Cu^+ in KCl, KBr, and KI and suggest that the excited Cu^+ ion relaxes toward the ideal lattice site. This phonomenon would explain their observation of a lower oscillator strength and a narrower line in emission than in absorption.

It is the purpose of this work to investigate within the framework of a point-ion model the possibility that Ag^+ and Cu^+ ions are off center in NaCl, KCl, RbCl, and RbBr and to compare these results with displacements deduced from oscillator-strength measurements. First the displacements of the impurity ions from their substitutional cation site and the minimum energy configuration of the surrounding ions for the various host crystals were determined. Then for Cu^+ in KCl, the oscillator strength of the $(3d)^{10} \rightarrow (3d)^9 4s$ transition was calculated using the model of a free Cu^+ ion in a strong crystalline field.

In Sec. II the method of calculation of the minimum energy configurations of Cu^+ and Ag^+ ions in various alkali halides is given. In Sec. III the results of these calculations are discussed, and finally in Sec. IV the oscillator strength of Cu^+ in KCl is calculated and the probable displacement evaluated.

II. METHOD OF CALCULATION OF DISPLACEMENTS

The total energy of the impurity-doped crystal relative to the perfect crystal is expressed as a function of displacement parameters assigned to ions neighboring the defect. The electrostatic and repulsive contributions to this total energy are calculated by the method of Hatcher and Dienes.[12] The electronic polarization energy can be approximated by considering the dipoles on each ion as being created only by the monopole distortion of the region about the defect and a dipole-dipole correction then added. However, one can eliminate this approximation by writing the polarization energy exactly as

$$E_{\text{pol}}=-\tfrac{1}{2}\sum_i \mathbf{P}_i\cdot\mathbf{E}_i\,, \tag{2.1}$$

where $\mathbf{E}_i$ is the field at ion i due to the monopoles only and $\mathbf{P}_i$ is the dipole on ion i due to both charges and dipoles on all other ions j in the crystal. That is,

$$\mathbf{P}_i=\alpha_i\mathbf{E}_i+\sum_j \frac{3\mathbf{r}_{ij}(\mathbf{P}_j\cdot\mathbf{r}_{ij})-\mathbf{P}_j}{|\mathbf{r}_{ij}|^5}\,, \tag{2.2}$$

where α_i is the polarizability of ion i and $\mathbf{r}_{ij}$ is the vector distance from ion i to ion j. Since $\mathbf{r}_{ij}(\mathbf{P}_j\cdot\mathbf{r}_{ij})=(\mathbf{r}_{ij}\mathbf{r}_{ij})\cdot\mathbf{P}_j$, Eq. (2) can be transformed into a set of linear equations in the unknown $\mathbf{P}_i$'s. Making use of the symmetry about the defect, one then reduces the number of unknowns and solves Eq. (2) by the usual techniques.

The approximate treatment of the polarization energy for an arbitrary set of displacement parameters turned out to be in error by about 12% as compared to the improved method. In all calculations described here this energy was determined by including 93 ions about the defect. Extending the polarizable region to 171 ions would have changed the results only by about 1%.

The most serious difficulty in this kind of calculation is the choice of suitable Born-Mayer repulsive constants for the impurity ion interactions. Mayer[13] has determined repulsive and van der Waals coefficients for the silver halides and Mayer and Levy[14] those for the cuprous halides by fitting the formulas to appro-

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priate experimental data. Ladd and Lee[15] more recently analyzed the Born-Haber cycle for the silver salts in the light of better experimental data and concluded that Mayer's model is inadequate. More important for our purposes is the fact that any fitting of parameters for the silver and copper salts may not reflect the interactions in a different host-lattice environment.

An independent experimental indication of the interaction between a silver (copper) and a halide ion in an alkali-halide lattice can be obtained indirectly from data of Kornfeld and Lemanov,[16] who have performed x-ray measurements of the latice constant of NaCl as a function of Ag^+, Br^-, and K^+ impurity ion concentration. Their results show that the introduction of K^+ produces the largest increase of the lattice parameter, Br^- produces a somewhat smaller increase, and Ag^+ produces a decrease in the lattice parameter. All these changes are proportional to the concentration of the impurities, and one can conclude that the Ag^+ creates the smallest local perturbation, that is, it fits into a normal lattice site more easily than does K^+ or Br^-. Dick and Das[17] and, more recently, Dick[18] have calculated the relaxations of host ions surrounding K^+ and Br^- impurities in NaCl. Dick's results show that the first nearest neighbors (fnn) to a K^+ ion in NaCl relax outward by 0.049–$0.051r_0$ and that a Br^- ion in NaCl produces a fnn outward relaxation of 0.026–$0.036r_0$, where r_0 is the interionic distance. Even in the crude approximation of attributing the lattice-constant change to a displacement of fnn only, Dick's results are in agreement with the x-ray experiments quoted above. Thus, on the same basis one can estimate the effect of Ag^+, with the result that Ag^+ in NaCl produces a fnn inward relaxation of about $0.015r_0$.

Choosing the Ag^+-Cl^- repulsive and van der Waals coefficients from Mayer,[13] we calculated the relaxations about a Ag^+ ion in NaCl. Second-nearest-neighbor Ag^+-Na^+ interactions were treated as purely point-ion interactions, a reasonable approximation for the more tightly bound positive ions. We obtained a fnn inward relaxation of $\sim 0.05r_0$, which is much bigger than the value deduced above from the x-ray data. It is interesting to note that Dreybrodt and Fussgaenger also found that the Mayer interactions gave no reasonable results.[4] If one neglects the van der Waals forces entirely, one obtains an inward relaxation of $0.013r_0$, in a much better agreement with experiment. Thus, we decided to use the Mayer and Mayer-Levy repulsive parameters for the Ag^+ and Cu^+ ions, but omit the van der Waals forces in all cases.

Interactions between ions in the host lattices were taken as usual from Tosi and Fumi.[19]

III. RESULTS

Following our early studies[20] of Li^+ in KCl, we assign three displacement parameters to 26 ions surrounding the defect when the Ag^+ or Cu^+ ion is fixed at a normal lattice site and 18 parameters to the same number of ions when the defect is allowed to relax along a $\langle 111\rangle$ direction. Unlike our method of Sec. IV of Ref. 20, we allowed all parameters in the $\langle 111\rangle$ configuration to vary rather than fixing the position of the impurity. As a result, when an ion is found to be on site, only one energy and three displacement parameters (assigned to first, second, and third nearest neighbors) are given. In this way, we obtain a better indication of the minimum energy configuration. It is recognized that further relaxation occurs in the region past the third nearest neighbors, but this is not expected to affect appreciably the relative energies of the various configurations.

Table I gives the energies and displacement parameters with the Ag^+ and Cu^+ ions fixed at normal cation sites in NaCl, KCl, RbCl, and RbBr. In Table II are listed the fnn displacements when the defect is allowed to relax along a $\langle 111\rangle$ direction. The notation of the displacements is as in Fig. 2(a) of Ref. 20. For NaCl:Ag, KCl:Ag, and RbBr:Ag the impurity did not go off center and hence these cases do not appear in Table II.

Good agreement with experiment was obtained for the Ag^+ impurities: Only in RbBr was Ag^+ found to be off center, the magnitude of its displacement being $0.096\sqrt{3}r_0 = 0.54$ Å, which is about twice that calculated by Dreybrodt and Fussgaenger.[4] Their calculations, however, allowed only the fnn to relax and should not be expected to give agreement with our results. It is to be noted that Ag^+ in RbBr was found to be on site, in agreement with electrocaloric measurements.[10] This is in contrast to Li^+ in KBr, where we found[20] the small impurity ion to be off center, while no electrocaloric effect was observed. This question of the off-center nature of Li^+ in KBr is still unsettled.[9]

For the Cu^+-doped crystals the agreement is less good. Cu^+ in NaCl, which is known to be on site or very nearly on site, we find from Table II to be displaced by $0.042\times\sqrt{3}\times 2.82$ Å$=0.21$ Å. Similarly, from Table II we find Cu^+ in KCl, RbCl, and RbBr to be off center by 1.36, 1.65, and 1.84 Å, respectively. As expected, the displacement from the center increases with the size of the lattice, so that Cu^+ is farther from the normal site in RbBr than in RbCl, unlike the Ag^+. It seems that covalent effects, which are neglected in our approximation, are playing a role in the Cu^+-Cl^-

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TABLE I. Energies and displacement parameters (in units of interionic distance) with the Ag^+ and Cu^+ ions fixed at normal cation sites.

Parameters P_i and energies (in eV)	NaCl:Ag	KCl:Ag	RbCl:Ag	RbBr:Ag	NaCl:Cu	KCl:Cu	RbCl:Cu	RbBr:Cu
P_1	−0.013	−0.069	−0.069	−0.045	−0.042	−0.087	−0.107	−0.095
P_2	−0.002	−0.010	−0.009	−0.006	−0.006	−0.013	−0.015	−0.012
P_3	0	0	0.002	0	0.002	0.002	0.002	0.002
E_{stat}	0.0018	0.0385	0.0705	0.0262	0.0238	0.1078	0.1817	0.1454
E_{pol}	−0.0011	−0.0281	−0.0404	−0.0165	−0.0117	−0.0609	−0.0995	−0.0762
E_{rep}	−0.4669	−1.0429	−1.1541	−0.7695	−0.9596	−1.3309	−1.4058	−1.2688
E_{tot}	−0.4662	−1.0325	−1.1240	−0.7598	−0.9475	−1.2840	−1.3236	−1.1996

(Cu^+-Br^-) interaction, particularly for large displacements and for larger ionic overlap.

Recognizing the approximation which we made in our treatment of the repulsive forces, we varied the Mayer-Levy hardness parameter in the Cu^+-Cl^- interaction by ±5% and found that this changed the displacement of the Cu^+ in KCl over the range 0.22–1.6 Å. Such sensitivity to the repulsive parameters is not unusual and is the reason why the study of off-center ions may lead to important conclusions concerning impurity ion interactions in solids.[21]

IV. OSCILLATOR STRENGTH OF KCl:Cu

Having shown that Ag^+ and Cu^+ ions can lie in off-center positions, we now calculate the oscillator strength of the $(3d)^{10} \rightarrow (3d)^9 4s$ absorption of Cu^+ in KCl. We choose a model for the Cu^+ center to be a free Cu^+ ion in a strong electric field directed along a $\langle 111 \rangle$ axis of the crystal, which hereafter will be called the z axis. Our model does not include the possibility of an electronic excitation of a covalent (Cu^+-$6Cl^-$) complex analogous to that considered[6] for KCl:Ag. So far as we know, no corresponding strong absorption band in KCl:Cu has been observed. Since according to experiment the oscillator strength is high and rather temperature-independent, we conclude that vibronic interactions are a lower-order effect and can be here neglected. This may not be true in other cases.

The electric field perturbs the $(3d)^{10}$ ground state (^1S) and the $(3d)^9 4s(^3D,{}^1D)$ by mixing in $(3d)^9 4p$-$(^3F,{}^3D,{}^3P,{}^1F,{}^1D,{}^1P)$ states. We neglect triplet states because the perturbation is spin-independent and the ground state is a singlet. For the perturbation $H' = Az$ the perturbed wave functions [rounded brackets, $|\cdots)$] are

$$|^1S) = |^1S\rangle - \frac{A\langle ^1S|z|^1P\rangle}{\epsilon_1+\epsilon_2}|^1P\rangle, \tag{4.1}$$

$$|^1D) = |^1D\rangle - \frac{A\langle ^1D|z|^1P\rangle}{\epsilon_2}|^1P\rangle - \frac{A\langle ^1D|z|^1F\rangle}{\epsilon_2-\sigma_3}|^1F\rangle, \tag{4.2}$$

where ϵ_1 is the energy difference $E[(3d)^9 4s,{}^1D] - E[(3d)^{10},{}^1S]$ and $\epsilon_2 = E[(3d)^9 4p,{}^1P] - E[(3d)^9 4s,{}^1D]$. The multiplet splitting $\sigma_3 = E(^1P) - E(^1F)$ is not needed because selection rules prohibit ^1F terms from entering into the oscillator-strength calculation. We neglect ^1F terms hereafter.

The $|^1P\rangle$ and $|^1D\rangle$ wave functions must be expressed as linear combinations of 10×10 determinants with p or s functions appropriately substituted for d functions. The coefficients in the linear combinations are the Clebsch-Gordan or vector-coupling coefficients. We treat the $(3d)^9 4s$ and $(3d)^9 4p$ configurations as d-s and d-p, where the d is a hole in the $(3d)^{10}$ shell and the $s(p)$ an electron. We then couple the orbital and spin angular momenta of d-p and d-s electrons and change the sign of the m_l and m_s values of the d electron to obtain those of the hole. We obtain

$$\begin{aligned} |3d^9 4s,{}^1D\rangle &= (1/\sqrt{2})[(0^-0^-)-(0^+0^+)], \\ |3d^9 4p,{}^1P\rangle &= [-2/(20)^{1/2}][(0^-0^-)-(0^+0^+)] \\ &\quad +(3/20)^{1/2}[(-1^- -1^-)-(-1^+ -1^+)] \\ &\qquad +(3/20)^{1/2}[(1^-1^-)-(1^+1^+)]. \end{aligned} \tag{4.3}$$

The parentheses within brackets represent 10×10 determinants, with the m_l value of the d hole appearing first and the corresponding m_s values given as superscripts (± implying $\pm\frac{1}{2}$). In the notation of Condon

TABLE II. Energies and displacement parameters (in units of interionic distance) with the Ag^+ and Cu^+ ions allowed to relax along a $\langle 111 \rangle$ direction.

Parameters P_i and energies (in eV)	RbCl:Ag	NaCl:Cu	KCl:Cu	RbCl:Cu	RbBr:Cu
P_1	0.096	0.042	0.250	0.290	0.310
P_2	0.096	0.049	0.079	0.109	0.109
P_3	−0.011	−0.001	0.025	0.005	0.015
P_4	−0.015	−0.029	0.033	0.053	0.043
P_5	0.001	−0.001	0.005	−0.015	−0.005
E_{stat}	−0.2650	0.0001	−0.7901	−0.8328	−0.2732
E_{pol}	−0.1535	−0.0997	−0.9257	−1.4719	−1.8545
E_{rep}	−0.7325	−0.8513	0.1304	0.1339	0.4526
E_{tot}	−1.1510	−0.9509	−1.5854	−2.1708	−1.6751

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and Shortley,[22]

$$(0^-0^-)=(2^+1^+0^+-1^+-2^+2^-1^--1^--2^-0^-),$$

with the d functions appearing first and the last entry a p or an s function.

If d_{m_l}, p_{m_l}, and s are normalized single-electron wave functions,

$$\langle{}^1S|z|{}^1P\rangle=(-2/\sqrt{5})\langle d_0|z|p_0\rangle-(\sqrt{\tfrac{3}{5}})\langle d_{-1}|z|p_{-1}\rangle \\ -(\sqrt{\tfrac{3}{5}})\langle d_{+1}|z|p_{+1}\rangle.$$

Furthermore, if $P_d(r)/r$, $P_p(r)/r$, and $P_s(r)/r$ are the radial functions, and we define

$$R_{sp}=\int_0^\infty rP_s(r)P_p(r)dr,$$

$$R_{pd}=\int_0^\infty rP_d(r)P_p(r)dr,$$

then it is a simple matter to show that

$$\langle{}^1S|z|{}^1P\rangle=-(\sqrt{\tfrac{4}{3}})R_{pd}. \tag{4.4a}$$

Similarily,

$$\langle{}^1D|z|{}^1P\rangle=-(2/15)^{1/2}R_{sp}. \tag{4.4b}$$

Combining Eqs. (4.1) and (4.2) with (4.4) we, obtain

$$\begin{aligned}|{}^1S)&=|{}^1S\rangle+A(\sqrt{\tfrac{4}{3}})[R_{pd}/(\epsilon_1+\epsilon_2)]|{}^1P\rangle,\\ |{}^1D)&=|{}^1D\rangle+A(2/15)^{1/2}(R_{sp}/\epsilon_2)|{}^1P\rangle.\end{aligned} \tag{4.5}$$

The oscillator strength f is proportional to the square of the dipole matrix elements between $|{}^1S)$ and $|{}^1D)$. For radiation whose electric vector is polarized along z we obtain

$$f=\frac{64\pi^2m\epsilon_1R_{sp}^2R_{pd}^2A^2}{45h^2}\left(\frac{1}{\epsilon_2}+\frac{1}{\epsilon_1+\epsilon_2}\right)^2. \tag{4.6}$$

The R_{sp} and R_{pd} values were calculated directly from the radial functions obtained from the Herman-Skillman program.[23] The results are

$$R_{sp}=-2.65\text{ a.u.},$$

$$R_{pd}=0.716\text{ a.u.}.$$

We used the experimental value of 4.75 eV [8] for ϵ_1, and took ϵ_2 to be approximately ϵ_1 by analogy with Ag^+.[2,3] Varying ϵ_2 in the range $0.9\epsilon_1\leq\epsilon_2\leq1.1\epsilon_1$ does not seriously affect the results. Since $A=eE$, where E is the electric field, we have

$$f=\frac{16\pi^2me^2R_{sp}^2R_{pd}^2E^2}{5h^2\epsilon_1}. \tag{4.7}$$

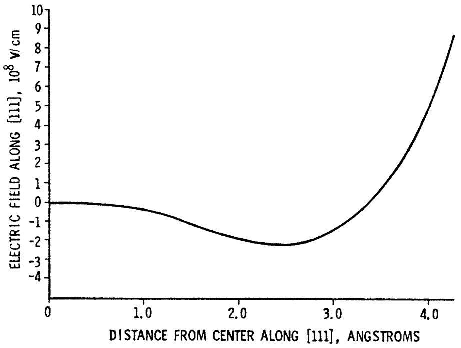

FIG. 1. Electric field along a ⟨111⟩ direction in KCl.

In Fig. 1 we have plotted the electric field along a ⟨111⟩ axis of a perfect KCl crystal by direct differentiation of the Ewald potential. Note that the field is quite small out to about 0.6 Å and changes sign as the ion approaches a nearest-neighbor Cl^- ion. This is a first-order approximation to the actual field seen by the impurity ion, since dipoles on other ions and covalent effects have been neglected. From Eq. (4.7) the oscillator strength will have the experimental value of 0.025 [7] when the field is about 2×10^8 V/cm. This requires the ion to be displaced from the ideal site by about 2 Å, in qualitative agreement with the large displacements calculated in Sec. III of this paper. It should be kept in mind, however, that the presence of a localized electronic excitation of a covalent complex mentioned above could reduce the magnitude of the required field and of the displacement considerably.[24] Dultz's value[8] of 0.3 Å would give an oscillator strength of only ~0.001, which would be comparable to a purely vibronic contribution. Therefore, it seems reasonable on both the point-ion model and the model used for the calculation of f that Cu^+ in KCl is displaced by about $\frac{1}{3}$ of the interionic distance along a ⟨111⟩ direction. For Cu^+ in NaCl, the 4% displacement would give rise to an oscillator strength of the order of 0.001, the same order of magnitude as that induced by electron-phonon interactions. Thus, in this case, it seems impossible to decide whether the ion is on site or slightly off by oscillator-strength measurements alone. Although no experimental results have been reported, we expect oscillator strengths for the $(3d)^{10}\rightarrow(3d)^94s$ transition to be about 0.05. Our results for Ag^+ in RbCl (0.54-Å displacement along ⟨111⟩) would also give a small contribution from field induced transitions because the field is still quite small at such distances (see Fig. 1).

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