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Ligand relaxation in copper- and silver-atom-doped alkali halides

M. T. Barriuso
Departamento de Física Teórica, Facultad de Ciencias, Universidad de Santander, Santander, Spain

M. Moreno
Departamento de Física Fundamental, Facultad de Ciencias, Universidad de Santander, Santander, Spain

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Through an analysis of the experimental isotropic superhyperfine constant A_s of Cu^0 and Ag^0 in several alkali halides, it is clearly demonstrated that significant outward ligand relaxations are involved in these cases. This analysis requiring accurate values of the overlap integral S_s allows one to estimate the true value of the impurity-ligand distance R. Such estimations point out that, for a given alkali chloride lattice, the Ag^0-Cl^- distance is about 0.10 Å larger than the Cu^0-Cl^- distance which is consistent with the higher size of Ag^0. The present work proves reasonably that, though $(R-R_0)/R_0$ (R_0 corresponding to the host lattice) can be up to 27%, the values of R follow those of R_0 through the series of alkali chlorides for both Cu^0 and Ag^0. This is also consistent with the reported analysis of the $(AgCl_5Br)^{6-}$ complex in KCl. Finally, the present work supports the idea that the ratio of the covalent contribution $\gamma p\sigma$ to the ligand $p\sigma$ admixture and the corresponding overlap contribution $S_{p\sigma}$ decreases when R decreases in the $(AgCl_6)^{6-}$ complex.

I. INTRODUCTION

The properties of a metallic substitutional impurity in an ionic lattice depend to a great extent upon the nature and geometric arrangement of the nearest anions.[1,2] To have a good insight, at a microscopic level, into the origin of the properties due to such an impurity one needs to know the true distance R between the impurity and its nearest neighbors.

In spite of its relevance, however, few works[1,3] have traditionally been devoted to this problem through the data provided by the standard experimental techniques such as EPR or optical absorption. Due to this, some not well-proven assumptions about the value of R have often been used in the interpretation of the experimental information.[4] It has been widely assumed, for instance, that R is close or equal to R_0 where R_0 corresponds to the cation-anion distance of the perfect lattice.[1,2,5–7]

Quite recently the advent of the more sophisticated extended x-ray absorption fine structure (EXAFS) technique is capable of giving good measurements of R. Nevertheless, this method often requires impurity concentrations around 1%,[8] much higher than those needed in the standard techniques by which true dilute solutions can be explored.

Owing to this, some efforts have been recently made to get information about R from EPR data[9,10] and the second-neighbor transferred hyperfine interactions measured in electron-nuclear double resonance (ENDOR) experiments.[11–14] It has been shown in this way[10] how an analysis of the isotropic superhyperfine (shf) constant A_s within a molecular-orbital scheme can offer good evidences about outward ligand relaxation due to a given paramagnetic impurity having weak bonding with its nearest anions. Moreover, a reasonable first estimation of R can also be achieved through such an analysis.[10]

In this paper we analyze, by means of that method, the experimental values of A_s for Cu^0 and Ag^0 in several alkali halides in order to detect possible outward relaxation effects and further to estimate how R varies along the different alkali halide lattices.

The substitutional Cu^0 and Ag^0 impurities in alkali halides have been chosen for the present study, firstly, because they exhibit weak bonding with the ligands[5,15–19] and, secondly, due to the good number of alkali chloride lattices where both impurities have been investigated.[15–17] Finally, ligand outward relaxation effects can be reasonably expected in the present cases in view of the much higher atomic radius of Cu^0 and Ag^0 with respect to that of the involved host cations.[20]

II. THEORETICAL

In Sec. II we report a brief outline on the method which, anyway, has been studied with more detail elsewhere.[10]

In the present cases the unpaired electron is placed on an antibonding a_{1g}^* level.[10,18] This mainly impurity level has σ bonding with the ligands. Within the molecular orbital (MO) scheme, the wave function of

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such a level can be shortly depicted as[10]

$$|a_{1g}^{*}\rangle = \alpha_M |n_M s\rangle - \lambda_{p\sigma}|\Phi_{p\sigma}\rangle - \lambda_s|\Phi_s\rangle \quad , \tag{1}$$

where $|n_M s\rangle$ is the valence s orbital of $\mathrm{Cu}^0(4s)$ or $\mathrm{Ag}^0(5s)$, while $|\Phi_{p\sigma}\rangle$ and $|\Phi_s\rangle$ mean suitable linear combinations of ligand $p\sigma$ and s orbitals, respectively. If the impurity is surrounded by six equivalent ligands, thus $\lambda_{p\sigma}^2 = 6f_\sigma$ and $\lambda_s^2 = 6f_s$, where f_σ and f_s, which can be determined experimentally, have their usual meaning.[1,2]

In a weak bonding situation having $\lambda_{p\sigma}^2$ and λ_s^2 much smaller than the unity, λ_s, for instance, is given by[1,10,21]

$$\lambda_s = \gamma_s + S_s \quad , \tag{2}$$

where $S_s = \langle n_M s|\Phi_s\rangle$ is a group overlap integral, rather sensitive to the value of R, while γ_s is the so-called covalent contribution which has the same sign as S_s. A similar expression happens for $\lambda_{p\sigma}$.[1,21]

Thus in a weak bonding situation, Eq. (2) implies that $\lambda_s^2 = 6f_s$, determined from the experimental A_s value, must be greater than or equal to $S_s^2(R)$ for the *true* value of R. In other words, if the "experimental" $6f_s$ value is less than $S_s^2(R_0)$, it means that a ligand outward relaxation process has necessarily taken place. Furthermore, as in the case of ligand halides, λ_s is clearly dominated by the overlap contribution S_s,[1,10,21–23] a first estimation of R can be achieved by looking at the value of R verifying[10]

$$S_s^2(R) = 6f_s \quad . \tag{3}$$

III. APPLICATIONS: DISCUSSION

In Sec. III the experimental A_s constants due to Cu^0 and Ag^0 in several alkali halides are analyzed by means of the method exposed in Sec. II. As such a method needs accurate values of the overlap integral S_s, we have employed for this purpose the corresponding free ion (or atom) Hartree-Fock-Roothaan wave functions by Clementi and Roetti.[24] The values of f_s have been deduced from the experimental values of A_s through the standard procedure.[1,2,10]

From Table I it becomes quite evident that both Cu^0 and Ag^0 give rise to significant outward ligand relaxations in all lattices. In fact, the ratio between $S_s^2(R_0)$ and $6f_s$ lies between 2.1 (for Cu^0:NaCl) and 3.3 (for Ag^0:LiCl), and so the experimental A_s values cannot be understood reasonably within the MO scheme unless an outward ligand relaxation has taken place.

The present systems can be roughly regarded as a cation vacancy filled with a neutral atom. Though a cation vacancy in an alkali halide gives rise to an outward ligand relaxation with $\Delta R/R_0$ being around 7%,[25,26] the estimated values for the present systems are much higher than this figure. This fact clearly suggests that the ligand outward relaxation in the present cases is mainly due to size effects of the impurity atom. This idea is in agreement with the fact that, for a given lattice, the estimated value of R for Ag^0 is slightly higher than that corresponding to Cu^0 in view of the higher size of the former. In this way, the difference between the atomic radius of free Ag^0 and Cu^0 is 0.19 Å,[20] while the difference between the estimated values of R for Ag^0 and Cu^0 in the same

TABLE I. The A_s values are referred to the mean chlorine or bromine isotope. These A_s values have been obtained by means of the EPR technique except those corresponding to Ag^0 in NaCl and KCl derived from ENDOR. R has been estimated through Eq. (3). ΔR means $R - R_0$.

Lattice	R_0 (Å)	Atom	A_s(10^{-4} cm^{-1}) Experimental	Reference	$6f_s$	$S_s^2(R_0)$	R (Å)	$\Delta R/R_0$(%)
LiCl	2.57	Cu^0	25.2	16	0.107	0.308	3.17	23.2
		Ag^0	26.5	17	0.112	0.368	3.27	27.2
NaCl	2.82	Cu^0	22.4	16	0.095	0.201	3.23	14.5
		Ag^0	22.1	15	0.094	0.242	3.37	19.3
KCl	3.15	Cu^0	10.3	16	0.044	0.110	3.63	15.2
		Ag^0	12.1	15	0.051	0.138	3.69	17.1
RbCl	3.29	Ag^0	9.8	17	0.042	0.108	3.80	15.3
KBr	3.30	Ag^0	73.4	19	0.062	0.138	3.75	13.5

lattice is 0.10, 0.14, and 0.06 Å for LiCl, NaCl, and KCl, respectively.

Table I clearly points out that, though R may be quite different from R_0, however, R follows the values of R_0 through the series of alkali chlorides for both Cu^0 and Ag^0 impurities. The accommodation of R to the value of R_0 had been suggested on some occasions.[2,6,7] The present work, however, offers a reasonable evidence of such a behavior.

On the other hand, the difference between the values of R for Ag^0 and Cu^0 in two different alkali chloride lattices follows the difference between the ionic radius of the involved host cations except in the case of LiCl. Likely, in this case a stronger $\Delta R/R_0$ value is needed in order to avoid a significant overlap between the electronic clouds of Ag^0 or Cu^0 and Cl^-.

As regards the value of f_σ, it usually increases when R decreases.[2,22,23] Thus one should expect from Table I that f_σ increases on going from Ag^0:RbCl to Ag^0:LiCl. Due to the smallness of the anisotropic shf constant A_p of Cu^0 and Ag^0 in alkali chlorides,[15–17] such a constant cannot be measured reliably by means of the EPR technique and thus only the cases of Table I studied by ENDOR provide us with accurate values of f_σ. In this way it is found $6f_\sigma$ to be equal to 0.168 and 0.216 for Ag^0:KCl and Ag^0:NaCl, respectively, in agreement with the expected trend. Anyway, these figures outline that a difference of about 0.30 Å in R induces small changes on f_σ. Further comments on this point are given later.

Recently Amanis *et al.*[27] succeeded in forming the $(\mathrm{AgCl_5Br})^{6-}$ complex within the KCl lattice. As R_0 in KCl is 0.14 Å smaller than in KBr, one should expect that the Ag^0-Br^- distance in such a complex would be less than that estimated for Ag^0:KBr. From the value of the bromine shf constant $A_s(\mathrm{Br}^-) = 92.1\times10^{-4}\ \mathrm{cm}^{-1}$ reported by Amanis *et al.* for the $(\mathrm{AgCl_5Br})^{6-}$ complex in KCl, we estimate a Ag^0-Br^- distance equal to 3.62 Å which is 0.13 Å smaller than that estimated for R in Ag^0:KBr. Moreover, the experimental results point out that the five Cl^- ions in the $(\mathrm{AgCl_5Br})^{6-}$ complex are practically equivalent, the chlorine shf constant being $A_s(\mathrm{Cl}^-) = 12\times10^{-4}\ \mathrm{cm}^{-1}$. From this figure a value of 3.69 Å is estimated for the Ag^0-Cl^- distance in such a complex. Thus the estimated values of the Ag^0-Cl^- and Ag^0-Br^- distances in the $(\mathrm{AgCl_5Br})^{6-}$ complex are consistent with the idea that the KCl lattice forces the Ag^0-Br^- distance to be smaller than in Ag^0:KBr though both the Ag^0-Br^- and the Ag^0-Cl^- distances in the $(\mathrm{AgCl_5Br})^{6-}$ complex are rather similar.

A situation quite close to the present one has been assumed in some tetrahedral ferric complexes.[28] In this way the absence of quadrupole effects in the Mössbauer spectra of $(\mathrm{FeCl_3Br})^-$, $(\mathrm{FeCl_2Br_2})^-$, and $(\mathrm{FeClBr_3})^-$ complexes has to be related to a geometrical arrangement of the ligands close to that of the tetrahedral $(\mathrm{FeCl_4})^-$ complex.[28]

It is clear from the discussion that the present method for estimating the value of R in weak bonding situations is founded on the fact that λ_s is mainly given by S_s in ligand halides. As regards the $p\sigma$-ligand admixture $\lambda_{p\sigma}$ into a_{1g}^*, the influence of the corresponding covalent contribution $\gamma_{p\sigma}$ upon $\lambda_{p\sigma}$ is more comparable to the overlap one $S_{p\sigma}$ because the ligand $p\sigma$ level is closer to the a_{1g}^* level than the ligand s level.[1,2,22]

Owing to this, an analysis of the anisotropic shf constant A_p, similar to that developed for the isotropic constant A_s, would give poorer results. In this sense even if $6f_\sigma$, derived from the experimental A_p value, is smaller than $S_{p\sigma}^2(R_0)$, however, the value of R calculated from the equation

$$S_{p\sigma}^2(R) = 6f_\sigma \tag{4}$$

should be smaller than that obtained through Eq. (3). From the values of f_σ already mentioned, we obtain by means of Eq. (4) $R = 3.26$ Å for Ag^0:NaCl while $R = 3.48$ Å for Ag^0:KCl, a fact which is in qualitative agreement with the preceding argument. It must be stressed, anyway, that R estimated through Eq. (4) is much closer to that estimated through Eq. (3) in the case of Ag^0:NaCl than in the case of Ag^0:KCl. This fact clearly suggests that the ratio $\gamma_{p\sigma}/S_{p\sigma}$ decreases when R decreases, though $\lambda_{p\sigma} = \gamma_{p\sigma} + S_{p\sigma}$ experiences a slight increase. This behavior is also in good agreement with recent theoretical calculcations about the $(\mathrm{MnF_6})^{4-}$ complex performed for different values of R.[23]

In conclusion, we believe that the present study offers a reasonable picture about outward ligand distorsions in Cu^0- and Ag^0-doped alkali halides. Of course a better knowledge about the ratio γ_s/S_s would improve the present estimations of R. In this way γ_s/S_s would increase on going from chlorine to bromine complexes in view of the smaller electronegativity of the later. Due to this the Br^--Ag^0 distances determined in the present work would be slightly underestimated with respect to the Cl^--Ag^0 distances. Further work along this line is currently under way.

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[1] J. Owen and J. H. M. Thornley, Rep. Prog. Phys. 29, 675 (1966).

[2] B. C. Tofield, J. Phys. (Paris) 37, C6-539 (1976).

[3] T. P. P. Hall, W. Hayes, R. W. H. Stevenson, and J. Wilkens, J. Chem. Phys. 38, 1977 (1963).

[4] M. Heming and G. Lehmann, Chem. Phys. Lett. 80, 235 (1981).

[5] P. G. Baranov, R. A. Zhitnikov, and N. I. Melnikov, Phys. Status Solidi 30, 859 (1968).

[6] J. J. Rousseau, A. Leblé, and J. C. Fayet, J. Phys. (Paris) 39, 1215 (1978).

[7] G. Lehman, J. Phys. Chem. Solids 41, 919 (1980).

[8] P. Rabe and R. Haensel, in *Festkörperprobleme: Advances in Solid State Physics,* edited by J. Treusch (Vieweg, Braunschweig, 1980), Vol. 20, p. 43.

[9] H. Murrieta, J. Rubio, and G. Aguilar, Phys. Rev. B 19, 5516 (1979); J. Rubio, H. Murrieta, and G. Aguilar, J. Chem. Phys. 17, 4112 (1979); H. Murrieta, G. Aguilar, and J. Rubio, J. Phys. C (in press).

[10] M. Moreno, J. Aramburu, and M. T. Barriuso, Phys. Lett. 87A, 307 (1982).

[11] R. Jeck and J. Krebs, Phys. Rev. B 5, 1677 (1972).

[12] C. Adam, A. Harker, and J. Owen, J. Phys. C 12, L239 (1979).

[13] R. DuVarney, J. Niklas, and J. M. Spaeth, Phys. Status Solidi B 103, 329 (1981).

[14] T. Yosida, J. Phys. Soc. Jpn. 49, 127 (1980).

[15] G. E. Holmberg, W. P. Unruh, and R. J. Friauf, Phys. Rev. B 13, 983 (1976).

[16] R. A. Zhitnikov, V. Koltsov, and N. Melnikov, Phys. Status Solidi 26, 371 (1968).

[17] P. G. Baranov, R. Zhitnikov, and N. Melnikov, Phys. Status Solidi 30, 851 (1968).

[18] M. Moreno, J. Phys. C 13, 6641 (1980); Chem. Phys. Lett. 76, 597 (1980).

[19] N. Melnikov, R. Zhitnikov, and P. G. Baranov, Fiz. Tver. Tela (Lenigrad) 13, 1337 (1971) [Sov. Phys. Solid State 13, 1117 (1971)].

[20] S. Fraga, J. Karwowski, and K. M. S. Saxena, *Handbook of Atomic Data* (Elsevier, Amsterdam, 1976), p. 465.

[21] S. Sugano, Y. Tanabe, and H. Kamimura, *Multiplets of Transition-Metal Ions in Crystals* (Academic, New York, 1970), p. 251.

[22] M. Moreno, Solid State Commun. 38, 1045 (1981).

[23] J. Emery, A. Leble, and J. C. Fayet, J. Phys. Chem. Solids 42, 789 (1981).

[24] E. Clementi and C. Roetti, At. Data Nucl. Data Tables 14, 177 (1974).

[25] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals,* 2nd ed. (Dover, New York, 1948), p. 61.

[26] G. Heder, J. M. Spaeth, and H. Harker, J. Phys. C 13, 4965 (1980).

[27] I. Amanis, J. Kliava, and J. Purans, Phys. Status Solidi B 89, 531 (1978).

[28] N. N. Greenwood and T. C. Gibb, *Mossbauer Spectroscopy* (Chapman and Hall, London, 1971), p. 154.