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Dependence of in-crystal ionic polarizabilities on ionic radii in doped isostructural series

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The variation of in-crystal ionic polarizabilities for isostructural series as a function of the host-ion radius is discussed from the standpoint of the exchange-charge model. The results support the findings of the point-charge-plus-induced-dipole model used in the analysis of Gd^{3+} spin-Hamiltonian parameters.

I. INTRODUCTION

Recently, Lewis and Misra[1,2] applied a point-charge-plus-induced-dipole (PCID) model to the analysis of the spin-Hamiltonian parameters of Gd^{3+} doping single crystals of $RCl_3 \cdot 6H_2O$ (rare-earth metal trichloride hexahydrates, hereafter RTH), where $R =$Nd, Sm, Eu, Tb, Dy, Ho, Er, and Tm, and of RF_3, $R =$La, Ce, Pr, and Nd. The model requires values for the polarizabilities of the various ions in the crystal. It is well known that these differ from the free-ion values. In particular, they will be different for different hosts (R^{3+}) in a given series, and will be further modified by the substitution of an impurity. In the application of the model, the free-ion values were taken as initial trial values and then these were varied, in a manner consistent with physical constraints, so as to get agreement with the reported experimental spin-Hamiltonian parameters. It was found that the resulting polarizabilities, for each ion type, varied linearly with the host rare-earth ion radius in each of the two series. More specifically, if one denotes the ionic radius of a given rare-earth host (R^{3+}) by r_R, and that of the substituted paramagnetic Gd^{3+} ion by r_{Gd}, it was found that the polarizability α was such that a plot of α vs Δr was linear with a negative slope ($\Delta r \equiv r_R - r_{Gd}$), for $\Delta r > 0$. For $\Delta r < 0$, this was also the case, except the slopes were smaller. (The case $\Delta r < 0$ applies only to RTH, since, for RF_3, $\Delta r > 0$ for all rare-earth ions considered in that series.) The purpose of this paper is to further justify this result on the basis of the exchange-charge model (ECM) of Dick and Overhauser.[3]

II. DETAILS

The basis of the ECM is as follows: In addition to other factors (see Refs. 1 and 2), the polarizability of an ion in a crystal depends on a nearest-neighbor short-range repulsive interaction due to the overlap of wave functions and associated Pauli-exclusion effects. This is modeled, in the ECM, as being equivalent to the presence of a positive exchange-charge distribution between the ions. The presence of this exchange charge results in a further deformation of the shells and, thus, to further polarization over and above that of the free ion, but of opposite sign. If a given ion A has occupied states U_i ($i=1, 2,\ldots,n_A$) and ion B has occupied states U_j ($j=1, 2,\ldots,n_B$), then the exchange charge between the ions is given by[3]

$$q_{\text{ex}} = 2\,|\,e\,|\,S_{ij}^2 \,, \tag{1}$$

where S_{ij} is the overlap integral:

$$S_{ij} = \int U_i(A) U_j(B) d\tau \,. \tag{2}$$

This is a two-center integral over all space and spin coordinates. The values of S_{ij} are critically dependent on the ion separation and are hence very sensitive to distortion effects such as those produced by the substitution of an under- or oversized paramagnetic ion in a host crystal.

The integrals S_{ij} have been evaluated by Löwdin[4] for LiCl and NaCl for a number of internuclear separations, but it is only recently that the specific effects of distortion have been examined. This has been done by Satoh *et al.*[5] They show that the electric dipole moment induced due to the presence of exchange charge may be written as a function of ϵ, where ϵ is the fractional change in the interionic separation produced by distortion. That is, if a_0 is the undistorted separation, and a is the distorted separation, then

$$a = a_0(1+\epsilon) \,. \tag{3}$$

The relation they give is

$$\mu = \xi + \eta\epsilon + \rho\epsilon^2 \,, \tag{4}$$

where μ is the dipole moment induced by the exchange charge, and ξ, η, and ρ are combinations of overlap integrals.

In their analysis of six alkali halides they found that $\xi \simeq -0.03$, $\eta \simeq +0.1$, and $\rho \simeq -0.5$. If one takes

$$\mu = \alpha E \ , \tag{5}$$

where α is the polarizability modified by the exchange effects, and E is the local electric field,[6] then from Eqs. (4) and (5)

$$\alpha = A + B\epsilon + C\epsilon^2 \ , \tag{6}$$

where it is assumed that A, B, and C have the same signs as ξ, η, and ρ, respectively.

Now, when one substitutes a paramagnetic ion (e.g., Gd^{3+}) into the host crystal (R^{3+}), the surrounding ions will tend to collapse towards the Gd^{3+} if the ionic radii are such that $r_R > r_{\mathrm{Gd}}$ (i.e., $\Delta r > 0$). Conversely, the surrounding ions will be forced away from their positions in the undoped lattice if $\Delta r < 0$. Thus, one should have the distortion-produced fractional change in the interionic separation, ϵ, varying as $-\Delta r$. If it is assumed, at least for small distortions, that this relation is linear, then one has

$$\epsilon \left[\equiv \frac{a - a_0}{a_0} \right] = -k \frac{\Delta r}{r_R} \ , \tag{7}$$

where k is a positive constant of proportionality. Returning to Eq. (6) and differentiating with respect to ϵ give

$$\frac{\partial \alpha}{\partial \epsilon} = B + 2C\epsilon \ . \tag{8}$$

If this equation is rewritten using ϵ as given by Eq. (7), one has

$$\frac{\partial \alpha}{\partial(\Delta r)} = -\left[\frac{k}{r_R}\right] B + 2\left[\frac{k}{r_R}\right]^2 C \Delta r \tag{9}$$

or

$$\frac{\partial \alpha}{\partial(\Delta r)} = -B' + C'\Delta r \ ,$$

where $B' > 0$ and $C' < 0$ (from the signs of η and ρ). Thus, for $\Delta r > 0$, one definitely has $\partial\alpha/\partial(\Delta r) < 0$. For $\Delta r < 0$, the sign of $\partial\alpha/\partial(\Delta r)$ will depend on the magnitude of C' relative to B' which may vary from crystal to crystal.

III. DISCUSSION

These results for the sign of $\partial\alpha/\partial(\Delta r)$ are the same as those reported above from the analysis of the PCID model. In Ref. 1, it was argued that, while the PCID model appears not to include short-range effects such as overlap and exchange, these effects are in fact built into the polarizability values. The analysis of this paper supports that contention.

In view of this, an *ab initio* approach (using the PCID model) to the problem of the ground-state crystal-field splitting of *S*-state ions, often considered prohibitive because of the complexities involved, becomes feasible. This is because one can now estimate the required polarizability values for ions embedded in crystals, as described previously.[1,2] That is, the values of the polarizability values predicted by the PCID model could conceivably be employed in future work to shed light on the role of overlap and covalency.

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[6] The term "local electric field" refers to the electric field at the site of the substituted ion produced by the other point charges and dipoles present in the rest of the crystal. This may be calculated explicitly employing Ewald's method, as in Ref. 1, using (distorted) ion positions and the polarizabilities estimated from free-ion values.