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Analysis of correlation effects in the crystal-field splitting of Nd^{3+}:$LaCl_3$ under pressure

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Spectroscopic data for Nd^{3+}:$LaCl_3$ at pressures up to 10 GPa are analyzed using a Hamiltonian containing one-electron crystal-field and two-electron correlation crystal-field operators. We find that the ratio of the correlation crystal-field parameter $G^4_{10A\,0}$ to the crystal-field parameter B^4_0 decreases from -0.9 at ambient pressure to -0.2 at 10 Gpa. This decrease is explained using the superposition model and the measured changes of the structural parameters under pressure. Our analysis suggests that the dependence of the correlation crystal-field interactions on the Nd^{3+}-Cl^- distance is much greater than the distance dependence of the one-electron crystal-field interactions.

I. INTRODUCTION

Though it has been very successful, the one-electron crystal-field (CF) model for the f^N configurations of lanthanide and actinide ions is not completely adequate. The model often gives a good fit to *most* of the data, but certain "anomalous" multiplets remain poorly fitted. The influence of correlation (many-electron) effects on crystal field splitting is reviewed in Ref. 1.

In previous investigations we have shown that the addition of certain correlation crystal-field (CCF) parameters $G^4_{10A\,Q}$ greatly reduce the fitting error for the $^2H(2)_{11/2}$ multiplet of Nd^{3+} in various host crystals.[2,3] The ratio of $G^4_{10A\,Q}$ to B^4_Q was found to be in the range -0.25 to -1, which is in agreement with the *ab initio* calculations of Ng and Newman,[4] who predicted a ratio of around -0.5 for Pr^{3+} in chloride crystals.

The one-electron crystal field of lanthanide ions in $LaCl_3$ under high pressure has been the subject of several recent studies.[5–8] In these investigations the superposition model[9] was used to explain the change in crystal-field parameters in terms of the pressure-induced changes in the structural parameters of the site. It was noted that the calculation of B^4_0 was particularly sensitive to the superposition-model parameter t_4, i.e., the distance dependence of the interaction.[5] Therefore, any difference between the distance dependence of the fourth-rank CF and CCF interactions should be particularly obvious for Nd^{3+}:$LaCl_3$.

II. CRYSTAL-FIELD FITS

The usual form of the one-electron crystal-field parametrization is

$$\mathcal{H}_{\mathrm{CF}} = \sum_{K,Q} B^K_Q \sum_i c^K_Q(\vartheta_i, \varphi_i), \tag{1}$$

where $c^K_Q(\vartheta_i, \varphi_i)$ is a spherical tensor operator for the ith f electron.

Judd[10] introduced a parametrization of correlation crystal-field effects using operators with well-defined transformation properties under Racah's parentage groups for the f shell:

$$\mathcal{H}_{\mathrm{OCCF}} = \sum_{i,K,Q} G^K_{iQ} g^{(K)}_{iQ}. \tag{2}$$

This parametrization has been discussed in Refs. 1, 2, and 11. Li and Reid[2] found that the parameters $G^4_{10A\,Q}$ were particulary important for the $^2H(2)_{11/2}$ multiplet of Nd^{3+}.

Thirty energy levels for Nd^{3+}:$LaCl_3$ have been determined by fluorescence spectroscopy at pressures from 0 GPa to 10 GPa.[8] We have carried out fits using the extensive data set of Ref. 12, where 127 energy levels were reported, plus one $^2H(2)_{11/2}$ level from Ref. 8, giving a total of 128 energy levels. The results are given in columns 1 and 2 of Table I. Free-ion parameters are omitted from the table. These are given in Ref. 8.

The smaller high-pressure data sets were fitted from pressures of 0 GPa to 10 GPa. The results for 0 GPa and 10 GPa, with and without the CCF parameter $G^4_{10A\,0}$, are given in columns 3–6 of Table I. The 0-GPa fits are quite similar to the 128-level fits. The CCF parameter $G^4_{10A\,0}$ decreases roughly linearly with pressure, from 245 cm^{-1} at 0 GPa to 55 cm^{-1} at 10 GPa, whereas B^4_0 is almost constant. The addition of $G^4_{10A\,0}$ has little effect on the one-electron crystal-field parameters.

The data set from the high-pressure study is much

TABLE I. Crystal-field and correlation crystal-field parameters (cm^{-1}) for Nd^{3+}:LaCl_3 at 0 GPa and 10 GPa.

	128 levels		30 levels			
	0 GPa		0 GPa		10 GPa	
	CF	CCF	CF	CCF	CF	CCF
	1	2	3	4	5	6
n	128	128	30	30	30	30
σ	9.2	8.6	8.2	5.7	7.5	7.6
$\sigma[^2H(2)_{11/2}]$	13.4	7.5	12.5	6.4	9.1	8.8
B^2_0	153(8)	153(7)	148(17)	159(12)	109(15)	112(16)
B^4_0	−345(14)	−325(13)	−286(22)	−281(15)	−271(20)	−270(20)
B^6_0	−722(14)	−722(13)	−686(20)	−697(13)	−935(18)	−937(18)
B^6_6	475(13)	471(12)	488(17)	478(12)	623(16)	621(16)
$G^4_{10A\,0}$		217(21)		245(17)		55(23)
$G^4_{10A\,0}/B^4_0$		−0.67(0.1)		−0.87(0.1)		−0.20(0.1)

smaller than the data sets used in previous work on CCF effects in Nd^{3+}.[2,3] Therefore, we must be careful to check that the decrease in $G^4_{10A\,0}$ is real. For the large (128-level) data set it is clear that $G^4_{10A\,0}$ is the most important CCF parameter. No other parameter is nearly so successful in reducing the deviation of not only the $^2H(2)_{11/2}$ multiplet, but also several others. This has been confirmed in several different compounds.[2,3] For the small data set available in the high-pressure study we cannot be so definite, and other parameters, notably $G^4_{10B\,0}$, $G^4_{2\,0}$, and $G^4_{3\,0}$, also improved the fit. However, whichever CCF parameter was added, the same decreasing trend with pressure was observed. As a test, we carried out some fits with the $^2H(2)_{11/2}$ multiplet removed. In this case $G^4_{10A\,0}$ still followed the same decreasing trend, but took on rather higher values. We are therefore confident that the decrease in $G^4_{10A\,0}$ is a real effect. In the next section we give an explanation using the superposition model.

III. SUPERPOSITION-MODEL CALCULATIONS

The superposition model has been widely used to analyze crystal-field and transition-intensity data,[9] and has already been used in previous studies of pressure effects in LaCl_3.[5] The basic assumption of the superposition model is that the interactions of the ion with each of its ligands are independent. We then consider the hypothetical parameter set which would be used if there were just *one* ligand, on the z axis at "reference" distance R_0. These are called *intrinsic* parameters. In the case of the crystal field these intrinsic parameters are $\bar{B}_K \equiv B^K_0$. If the actual ligand coordinates are (R_L, Θ_L, Φ_L), the parameters can be expressed in terms of spherical harmonics of those coordinates. In the case of the crystal-field parameters this becomes

$$B^K_Q = \sum_L \bar{B}_K\, C^K_{-Q}(\Theta_L, \Phi_L)\,(-1)^Q \left(\frac{R_0}{R_L}\right)^{t_k}, \tag{3}$$

where t_k represents the distance dependence of the interaction.

We can use the superposition model to calculate the crystal-field parameter B^4_0 or the correlation crystal-field parameter $G^4_{10A\,0}$. In either case the parameter will be equal to the "intrinsic" parameter $\bar{B}_4(R_0)$ or $\bar{G}^4_{10A}(R_0)$, multiplied by the geometrical factor

$$\mathcal{G}_{40} = \frac{3}{4}\left[[35\cos^4\Theta - 30\cos^2\Theta + 3]\left(\frac{R_0}{R_A}\right)^{t_4} + \frac{3}{2}\left(\frac{R_0}{R_E}\right)^{t_4}\right], \tag{4}$$

where Θ, R_A, and R_E are angular and radial coordinates of the ligands, defined in Ref. 5. Θ, R_A, and R_E have been determined in Ref. 5 by x-ray diffraction. Using these functions we can calculate $\mathcal{G}_{40}$ as a function of pressure and the radial dependence factor t_4. Of course, there is no reason why t_4 should be the same for B^4_0 and $G^4_{10A\,0}$.

In Fig. 1, we plot $\mathcal{G}_{40}$ as a function of pressure and t_4, scaled to unity at 0 GPa. We see that a choice of t_4 of less than 5 gives only a small reduction in magni-

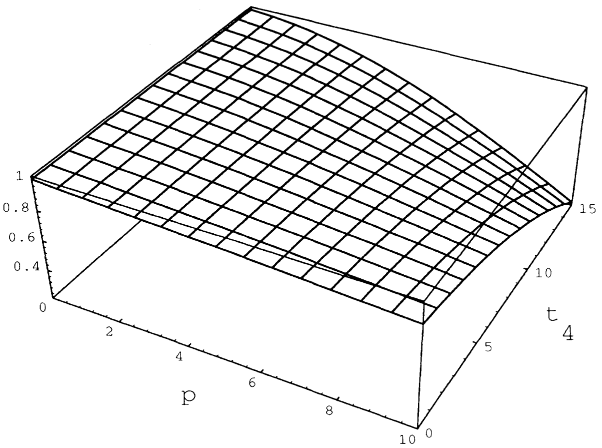

FIG. 1. Superposition-model factors $\mathcal{G}_{40}$ for B^4_0 or $G^4_{10A\,0}$ [see Eq. (4)] as a function of pressure p (in GPa) and power-law dependence t_4 scaled to unity at 0 GPa.

tude as p increases, which is the case for B_0^4, whereas a t_4 close to 15 gives the large reduction determined for $G_{10A\,0}^4$. Thus, the experimental data can be explained if the dependence of the CCF interaction with distance is quite different from the dependence of the one-electron CF interaction. Note that, because of local distortions, there are considerable errors in the determination of the structural parameters.[5] However, the determination of the relative changes in these parameters, on which the geometrical factor $\mathcal{G}_{40}$ depends, is much more certain.

IV. CONCLUSIONS

This is the first study of the effect of pressure-induced variations on correlation crystal-field effects in lanthanide ions, and the results are quite surprising. The CCF parameter $G_{10A\,0}^4$ in Nd^{3+}:$LaCl_3$ changes dramatically with pressure, whereas the one-electron parameter B_0^4 does not. This is explicable within the context of the superposition model and the change of the structural parameters with increasing pressure, if we may assume that the CF and CCF interactions have very different distance dependences. This suggests that our earlier work,[2,3,11] where we assumed that the distance dependence of the CF and CCF interactions was similar, may require some revision.

The *ab initio* study of Ng and Newman[4] did not address the distance dependence of the CCF interactions, and we have no simple mechanistic explanation of our results. Studies of other ions with known "anomalous" multiplets, such as $^1D_2$ of Pr^{3+} or $^3K_8$ of Ho^{3+}, would be very interesting.

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