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EPR spectrum of coupled pairs of Gd^{3+} ions in single crystals of $CsCdBr_3$

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The EPR spectrum of crystals of $CsCdBr_3$ doped with small amounts of Gd^{3+} ($\simeq$0.1-at.% Gd^{3+}) is dominated by resonances arising from weakly coupled pairs. The analysis of the spectrum shows the exchange interaction to be antiferromagnetic but extremely weak ($J=+0.00068$ cm^{-1}). The pair seems to consist of two Gd^{3+} ions associated with a Cd^{2+} ion vacancy. The unusual stability of this type of pair apparently arises from the charge balance requirements of the $CsCdBr_3$ lattice which has a linear-chain $CsNiCl_3$-type structure. The formation of Gd^{3+}-Gd^{3+} pairs in the $CsCdBr_3$ crystals can be inhibited by the presence of other trivalent ions and small monovalent ions.

Recently it has been shown by electron paramagnetic resonance (EPR) that crystals of $CsMgCl_3$ doped with trivalent chromium contain unexpectedly large concentrations of $Cr^{3+}-Cr^{3+}$ pairs.[1] It was suggested that the unusual tendency to cluster in pairs might be exhibited by other trivalent ions when introduced into the $CsMgCl_3$ lattice. The host material belongs to a large series of AMX_3 halides which adopt the hexagonal $CsNiCl_3$ structure.[2] We now wish to report the results of an EPR study of crystals of $CsCdBr_3$ containing trivalent gadolinium. ($CsCdBr_3$ also adopts the $CsNiCl_3$ structure.[3]) As was the case with $CsMgCl_3$ doped with Cr^{3+}, the EPR spectrum of crystals of $CsCdBr_3$ containing Gd^{3+}($\simeq$0.1-at.% Gd^{3+}) is dominated by resonances from weakly coupled pairs. Analysis of the spectrum gives a direct measure of the magnetic exchange and dipolar interactions between the two Gd^{3+} ions in the coupled pair. The results of this study indicate that trivalent ions will, in general, tend to aggregate in pairs when doped into a host lattice which adopts the $CsNiCl_3$ structure. This study also shows that the distribution of a particular trivalent ion in this type of host lattice can be profoundly affected by the presence of other trivalent and monovalent impurities.

In $CsMgCl_3$ and $CsCdBr_3$ each divalent metal ion is surrounded by an octahedron of halide ions. The octahedral MX_6^{4-} units are arranged in infinite arrays forming linear chains of octahedra sharing opposite faces. The chains, which run parallel to the crystallographic c axis, are negatively charged and have the overall stoichiometry $(MX_3^-)_n$. The Cs^+ ions balance the charge and occupy positions between chains. It was determined that the $Cr^{3+}-Cr^{3+}$ pair which occurs in high concentrations in the doped $CsMgCl_3$ crystals consists of two Cr^{3+} ions associated with a Mg^{2+} ion vacancy.[1] The Cr^{3+} ions occupy Mg^{2+} ion sites on either side of the vacancy to produce a linear Cr^{3+}-vacancy-Cr^{3+} system which runs along the $(MgCl_3^-)_n$ chain. The Gd^{3+}-Gd^{3+} pairs which are observed in the spectrum of the doped $CsCdBr_3$ crystals appear to have a structure which is analogous to that of the Cr^{3+}-Cr^{3+} pairs (see Fig. 1). It is clear that this type of pair occurs far more frequently than would be predicted from simple statistical considerations. This indicates that there is a unique stability associated with the arrangement of ions in the pair. The stability of the arrangement presumably arises from the charge balance requirements of the linear chain $CsMX_3$ lattice. The substitution of a trivalent ion in place of a divalent ion usually requires some mode of charge compensation. The combination of

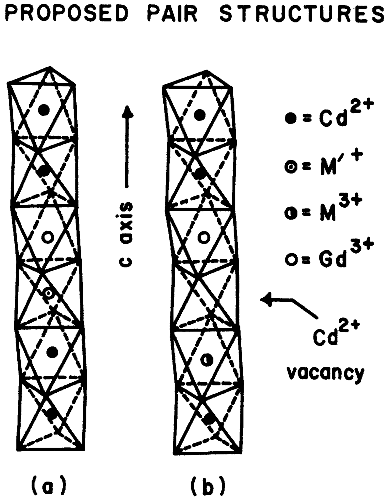

FIG. 1. Proposed structures of the Gd^{3+}-containing systems in $CsCdBr_3$. Combination of a Gd^{3+} ion with a small monovalent ion is shown in (a). Combination of a Gd^{3+} ion with a second trivalent ion (In^{3+} or Gd^{3+}) is shown in (b).

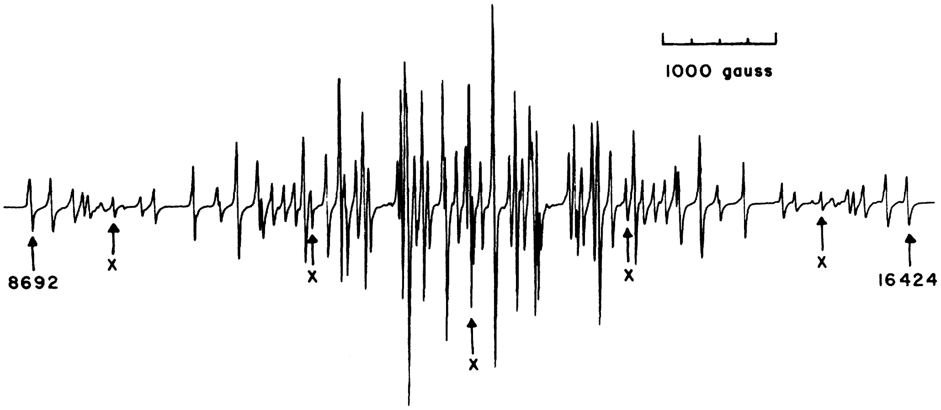

FIG. 2. Room-temperature EPR spectrum of a crystal of $CsCdBr_3$ doped with Gd^{3+}. Spectrum was taken with the field parallel to the *c* axis at a frequency of 35.01 GHz. Resonances marked with an **X** arise from a species containing a single Gd^{3+} ion. Remainder of the resonances arise from the Gd^{3+}-Gd^{3+} pairs.

two trivalent ions and a vacancy allows trivalent ions to be incorporated into an $(MX_3^-)_n$ chain without changing the total charge.

The EPR spectrum of the Gd^{3+} - Gd^{3+} pairs is quite complex. Even when the magnetic field is applied parallel to the crystallographic *c* axis more than 70 lines are clearly resolved (see Fig. 2). The spectrum has certain characteristics which are similar to those reported by Wolf and co-workers for Gd^{3+} - Gd^{3+} pairs in crystals of $LaCl_3$ and $EuCl_3$.[4-6] They showed that the spectrum of a coupled pair of Gd^{3+} ions can be described by a spin Hamiltonian of the following form:

$$\mathcal{H} = \mathcal{H}^p + \mathcal{H}_1^s + \mathcal{H}_2^s \ .$$

The magnetic interactions between the two ions are included in $\mathcal{H}^p$ while the single-ion, Zeeman, and crystal-field terms are contained in $\mathcal{H}_1^s$ and $\mathcal{H}_2^s$. If the two Gd^{3+} ions are equivalent, $\mathcal{H}_1^s$ will be equal to $\mathcal{H}_2^s$. For a pair of Gd^{3+} ions which are fairly far apart only exchange and dipole-dipole interactions should be significant. Thus, $\mathcal{H}^p$ can be written

$$\mathcal{H}^p = J(\vec{S}_1 \cdot \vec{S}_2) + \alpha(\vec{S}_1 \cdot \vec{S}_2 - 3S_{1z}S_{2z}) \, .$$

The *J* and α constants represent the parameters for isotropic exchange and dipole-dipole coupling, respectively. Wolf and co-workers showed that a pair spectrum could be interpreted by considering only the crystal-field terms that are diagonal when the field is parallel to the Gd^{3+}-Gd^{3+} axis.[5] An appropriate single-ion Hamiltonian for a Gd^{3+} ion is as follows:

$$\mathcal{H}^s = g\mu_B H_Z S_Z + \tfrac{1}{3} b_2^0 O_2^0 + \tfrac{1}{60} b_4^0 O_4^0 + \tfrac{1}{1260} b_6^0 O_6^0 \ .$$

It is clear that a complete interpretation of a pair spectrum requires some knowledge of these single-ion parameters. For this reason a series of experiments were carried out in an effort to produce $CsCdBr_3$ crystals containing "isolated" Gd^{3+} ions.

Since the distribution of Gd^{3+} ions in the $CsCdBr_3$ lattice appears to be determined by electrostatic rather than chemical or magnetic factors, it was assumed that this distribution could be affected by the presence of other impurities. Crystals of $CsCdBr_3$ doped with Gd^{3+} and either Na^+ or Li^+ were prepared and studied. In both cases the complex pair resonance is greatly reduced in intensity and a simpler resonance appears which is characteristic of a single Gd^{3+} ion in an axial site. Clearly these small monopositive ions provide an alternate mode by which the Gd^{3+} ions can be incorporated into the $CsCdBr_3$ lattice. It seems likely that the Gd^{3+} ion enters the host lattice in combination with a Li^+ or Na^+ ion. If two Cd^{2+} ions in adjacent sites along one of the $(CdBr_3^-)_n$ chains are replaced with a trivalent and a monovalent ion, the overall charge balance of that chain is retained [see Fig. 1(a)]. As was the case with Li^+ and Na^+ the formation of Gd^{3+}-Gd^{3+} pairs is inhibited by the presence of trivalent indium. Crystals of $CsCdBr_3$ doped with both Gd^{3+} and In^{3+} exhibit a spectrum characteristic of a single Gd^{3+} ion. In this case the In^{3+} and Gd^{3+} ions apparently form a "mixed" pair which has the same basic structure as the Gd^{3+}-Gd^{3+} pair [see Fig. 1(b)]. The diagonal terms in the spin Hamiltonian were determined for the three types of single Gd^{3+} ions from the spectra which were recorded with the magnetic field parallel to the crystallographic *c* axis. These parameters are given in Table I.

The parameters of the Gd^{3+}-In^{3+} system were assumed to give the best estimate of the single-ion parameters for the Gd^{3+}-Gd^{3+} pair since the Gd^{3+} ion environment is similar in these two systems. Using the Gd^{3+}-In^{3+} parameters as a starting point, the spectrum of the Gd^{3+}-Gd^{3+} pairs was analyzed following the procedure outlined by Wolf and co-workers.[4-6] Since all of the pairs in the $CsCdBr_3$ crystals are oriented along the $(CdBr_3^-)_n$

TABLE I. Spin-Hamiltonian parameters of the various Gd^{3+} containing systems in CsCdBr$_3$ at room temperature.

Parameter[a]	Gd^{3+} – Li^{+}	Gd^{3+} – Na^{+}	Gd^{3+} – In^{3+}	Gd^{3+} – Gd^{3+}
g	1.991(5)	1.991(1)	1.991(1)	1.991(1)
J (cm^{-1})	...	...	...	+0.000 68(8)
α (cm^{-1})	...	...	...	+0.007 81(8)
b_2^0 (cm^{-1})	± 0.0336(2)	± 0.037 02(10)	± 0.041 01(10)	+0.042 32(10)
b_4^0 (cm^{-1})	± 0.0029(1)	± 0.002 90(3)	± 0.002 69(3)	+0.002 69(3)
b_6^0 (cm^{-1})	± 0.0003(1)	± 0.000 22(3)	± 0.000 19(3)	+0.000 17(5)

[a] The number in parentheses corresponds to the estimated maximum error in the reported parameter.

chains, the analysis was carried out on the spectrum which is obtained when the field is applied parallel to the c axis. The spectrum is approximately symmetric about the center field of the resonance (H_0). For each peak in the low-field portion of the spectrum there is a corresponding peak which appears in the high-field half. As was pointed out by Wolf and co-workers the presence of a large number of lines makes it possible to determine the spin-Hamiltonian parameters with a great deal of precision. The parameters for the Gd^{3+}-Gd^{3+} pair are given in Table I. (The signs of

TABLE II. Experimental and calculated line shifts (in G) for the Gd^{3+} – Gd^{3+} pairs in CsCdBr$_3$ at room temperature.

ΔH_{expt}[a]	ΔH_{calc}	Difference	ΔH_{expt}[a]	ΔH_{calc}	Difference
25	33	–8	1834	1829	+ 5
105	106	–1	1859	1853 1868	–1
215	212	+ 3			
			2050	2051	–1
222	222	0			
			2205	2202	+ 3
363	360	+ 3			
			2218	2220	–2
416	413	+ 3			
			2441	2441	0
476	477	–1			
			2781	2782	–1
598	595	+ 3			
			2898	2898	0
621	624	–3			
			3046	3056	–10
882	875	+ 7			
			3227	3227	0
930	926	+ 4			
933	939	–6	3356	3360 3363	–5
993	995	–2	3405	3405	0
1093	1084 1099	+ 2	3491	3488 3504	–5
1142	1136 1139	+ 4	3685	3686 3690	–3
1460	1458	+ 2	3866	3867	–1
1541	1536	+ 5	4904	4897	+ 7
1635	1631	+ 4			

[a] ΔH_{expt} values were obtained by averaging the observed shift from center field, $|H_{\text{res}} - H_0|$, of each resonance in the low-field half of the spectrum with the shift observed for the corresponding resonance in the high-field half. The spectrum was taken at a frequency of 35.01 GHz. The center field, H_0, is 12 557 G.

the parameters are based on the assumption that α is positive.) The agreement between the observed line positions and those calculated from the calculated parameters is shown in Table II. The data are presented in terms of the amount, ΔH, each peak is shifted from the center field (H_0). The data for the high- and low-field halves of the spectrum are averaged. The overall agreement is excellent.

The data show that the exchange interaction between the two Gd^{3+} ions in the pair is antiferromagnetic, but extremely weak. The isotropic exchange parameter, J, is more than an order of magnitude less (in absolute value) than any of those measured for the Gd^{3+}-Gd^{3+} pair systems which occur in $LaCl_3$ and $EuCl_3$.[5,6] It seems likely that the exchange interaction is weak in the case of the pairs in $CsCdBr_3$ because the two Gd^{3+} ions are fairly far apart and there are no direct superexchange pathways. A reasonably accurate estimate of the distance between the two Gd^{3+} ions can be obtained from the dipolar term, α. For a pair of Gd^{3+} ions the dipolar interactions can be fairly well described by the following point-dipole expression:

$$\alpha = +g^2\mu_B^2/R^3 \ .$$

Using the measured value of α, an interionic separation, R, of 6.0 Å can be calculated. This distance can be compared with the value of 6.70 Å for the separation of next-nearest-neighbor Cd^{2+} ions in the host lattice. Since a Cd^{2+} vacancy creates an excess of negative charge, it seems quite likely that the two Gd^{3+} ions in the pair system will be attracted toward the vacancy. Thus, a Gd^{3+}-Gd^{3+} separation which is somewhat smaller than that predicted from the structure of the unperturbed host lattice seems quite reasonable.

While the properties of the Gd^{3+}-Gd^{3+} pairs are interesting in their own right, the most significant conclusion to be drawn from this study is that trivalent ions will, in general, tend to cluster in pairs when doped into a host lattice which adopts the linear chain $CsNiCl_3$ structure. This conclusion is supported by the fact that ions as different as Cr^{3+} and Gd^{3+} behave in the same manner. (Recent studies in our laboratories show that Cr^{3+} clusters in pairs when doped into crystals of $CsMgBr_3$ and $CsCdBr_3$ as was observed in $CsMgCl_3$.) It seems certain that pair systems of a variety of trivalent ions can be prepared by using the $CsMX_3$ salts as host lattices. The situation is quite unique in that the concentration of pairs is large compared with those of isolated ion species, even when the level of doping of the trivalent ion is fairly low (≃0.1 at.%). The fact that the distribution of a trivalent ion can be manipulated by the introduction of other impurities into the $CsMX_3$ lattice provides a valuable experimental means for controlling the nature of the spectroscopic species present in the doped crystals.

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