PHYSICAL REVIEW B VOLUME 16, NUMBER 11 1 DECEMBER 1977

EPR spectra of magnetically coupled pairs of Gd^{3+} ions in crystals of $CsMgCl_3$, $CsMgBr_3$, and $CsCdBr_3$

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(Received 18 July 1977)

The EPR spectra of crystals of $CsMgCl_3$, $CsMgBr_3$, and $CsCdBr_3$ doped with Gd^{3+} are dominated by resonances arising from weakly coupled pairs. The host materials all adopt the linear-chain $CsNiCl_3$ structure. The exchange interactions between the Gd^{3+} ions within the pairs are antiferromagnetic but extremely weak. At room temperature, the exchange parameter J for the pair in $CsMgCl_3$, $CsMgBr_3$, and $CsCdBr_3$ is equal to $+0.00107$, $+0.00080$, and $+0.00068$ cm^{-1}, respectively. The pairs consist of two Gd^{3+} ions associated with a Mg^{2+} or Cd^{2+} ion vacancy. The unusual stability of this type of pair apparently arises from the strict charge-compensation requirement of the linear-chain $CsMX_3$ lattice.

I. INTRODUCTION

In an earlier report it was shown that trivalent gadolinium ions have an unusual tendency to cluster in pairs when doped into crystals of $CsCdBr_3$.[1] Since that time it has become quite apparent that this sort of behavior is characteristic of trivalent ions which have been introduced as impurities into $CsCdBr_3$ and other structurally similar halide salts.[1-3] The host materials have the general formula $CsMX_3$ and adopt the hexagonal $CsNiCl_3$ structure. This structure can be described as an array of infinite parallel chains composed of MX_6^{4-} octahedra sharing opposite faces. The chains are negatively charged and have the overall stoichiometry $(MX_3^-)_n$. The Cs^+ ions occupy positions between the chains and serve to balance the negative charge. The tendency of trivalent impurities to aggregate in pairs appears to result from the rather strict charge-compensation requirement of the linear-chain $CsMX_3$ lattice. The pairs consist of two trivalent ions which occupy divalent metal-ion sites within a single $(MX_3^-)_n$ chain. These two sites lay on either side of a divalent metal-ion site that is vacant, forming a linear M^{3+}-vacancy-M^{3+} system (see Fig. 1). The combination of a vacancy and two trivalent ions provides a means by which the trivalent impurities are incorporated into the MX_3^- chains without disrupting the overall charge balance. This paper presents the results of an analysis of the EPR spectra of the Gd^{3+}-Gd^{3+} pairs in crystals of $CsMgCl_3$ and $CsMgBr_3$ as well as a more complete discussion of the Gd^{3+}-Gd^{3+} pairs in $CsCdBr_3$. The spectroscopic and magnetic properties of the coupled pairs in the three host lattices are compared with other Gd^{3+}-Gd^{3+} systems.

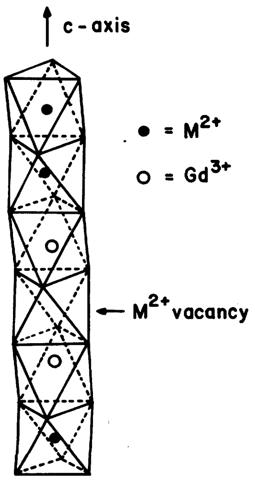

FIG. 1. Perspective view of a single MX_3^- chain from a $CsMX_3$ salt showing the proposed structure of the Gd^{3+}-Gd^{3+} pair system. The M^{2+} ions correspond to either Mg^{2+} or Cd^{2+}. The corners of the octahedra are occupied by halide ions.

II. EXPERIMENTAL

A. Preparation of materials

The host materials $CsMgCl_3$ and $CsCdBr_3$ were prepared according to previously described procedures.[4,5] The $CsMgBr_3$ was formed by fusing cesium bromide and anhydrous magnesium bromide together in evacuated Vycor ampuls. The anhydrous $MgBr_2$ was prepared by the direct reaction of the elements at 650°C. The Gd^{3+}-doped samples were made by adding a small amount (less than 0.1 wt.%) of GdI_3 to the host materials. These mixtures were then fused in Vycor ampuls under a partial pressure of the appropriate halogen vapor (either Cl_2 or Br_2). The purpose of the halogen vapor was to chemically replace the iodide ions in the mixtures which come from the GdI_3. Single crystals were grown from the melt by the Bridgman method. The apparatus and procedure have been previously described.[6]

B. EPR spectra

The $CsMX_3$ crystals have a strong tendency to cleave parallel to the crystallographic c axis. This greatly facilitates mounting and orienting samples for EPR study. Most crystals were mounted so that the magnetic field could be aligned parallel to the *c* axis. Spectra were studied at 9.5 GHz on a Varian E-3 spectrometer and at 35 GHz on a Varian E-12 spectrometer. Both instruments use 100-KHz field modulation. Magnetic fields were determined with a Spectromagnetic Industries gaussmeter.

III. RESULTS AND DISCUSSION

All three of the host materials used in this study have been characterized to some extent by x-ray diffraction. Complete structural analyses of $CsMgCl_3$ and $CsMgBr_3$ have been carried out,[4,7] while the unit-cell constants and probable space group of $CsCdBr_3$ have been determined.[5] The data clearly indicate that $CsMgCl_3$, $CsMgBr_3$, and $CsCdBr_3$ belong to a fairly extensive series of AMX_3 halides which adopt the linear-chain $CsNiCl_3$ structure. The structural studies of $CsMgCl_3$ and $CsMgBr_3$ show the magnesium ions to be surrounded by somewhat distorted octahedra of halide ions. The distortion corresponds to an elongation along the threefold axis of the $(MgX_3^-)_n$ chain. This elongation seems to be a common feature of the structures of the linear-chain AMX_3 halides.[5] Apparently the electrostatic repulsion between the divalent metal ions causes the $(MX_3^-)_n$ chains to stretch out noticeably from idealized octahedral geometry. Although the exact structural details of $CsCdBr_3$ have not been determined, it is almost certain that the structure closely resembles that of $CsMgCl_3$ and $CsMgBr_3$. One important structural parameter which can be calculated directly from the lattice constants is the separation between metal ions within the $(MX_3^-)_n$ chains. The nearest-neighbor M^{2+}-M^{2+} distance is equal to one-half of the lattice constant *c*. Thus, the Mg^{2+}-Mg^{2+} separation in $CsMgCl_3$ is 3.09 and 3.25 Å in $CsMgBr_3$, while the Cd^{2+}-Cd^{2+} distance in $CsCdBr_3$ is 3.35 Å. From a spectroscopic point of view, $CsMgCl_3$, $CsMgBr_3$, and $CsCdBr_3$ are ideal host materials because of the high symmetry and uniaxial character of the $CsMX_3$ lattice.

As was reported earlier, the EPR spectrum of $CsCdBr_3$ crystals doped with gadolinium is dominated by the resonances arising from a weakly coupled pair of Gd^{3+} ions.[1] The same phenomenon is observed when crystals of $CsMgCl_3$ and $CsMgBr_3$ are doped with gadolinium. The Gd^{3+}-Gd^{3+} pairs which contain 14 unpaired electrons produce extremely complex EPR spectra. Figures 2 and 3 show the EPR spectra of Gd^{3+} in crystals of $CsMgCl_3$ and $CsCdBr_3$ recorded with the magnetic field parallel to the crystallographic *c* axis. The similarity of the two spectra is quite apparent in spite of the complex appearance. The spectrum of Gd^{3+} in crystals of $CsMgBr_3$ is basically the same. All three spectra can be successfully analyzed in terms of the theoretical treatment outlined by Hutchings, Birgeneau, and Wolf.[8] The spectrum of a Gd^{3+}-Gd^{3+} is described by a spin Hamiltonian of the form

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

The magnetic interactions between the two ions are contained in $\mathcal{H}^p$, while the Zeeman and crystal field terms for the two ions are included in $\mathcal{H}_1^s$ and $\mathcal{H}_2^s$. 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

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

where the constants J and α represent the parameters for isotropic exchange and dipole-dipole coupling, respectively. If the two ions are equivalent, the single-ion Hamiltonians $\mathcal{H}_1^s$ and $\mathcal{H}_2^s$ are the same. It is possible to determine the impor-

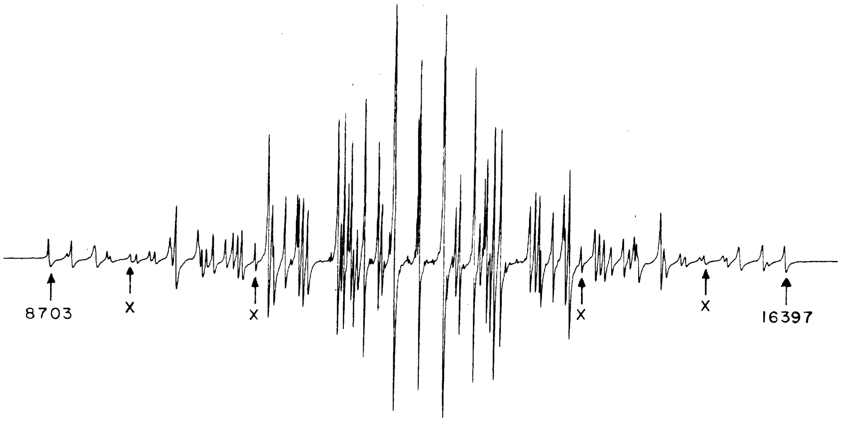

FIG. 2. EPR spectrum of a crystal of $CsMgCl_3$ doped with Gd^{3+}. The spectrum was recorded at room temperature with the field parallel to the crystallographic *c* axis. The frequency was 35.03 GHz. The resonances marked by × correspond to an isolated Gd^{3+} spectrum. The magnetic fields are given in gauss.

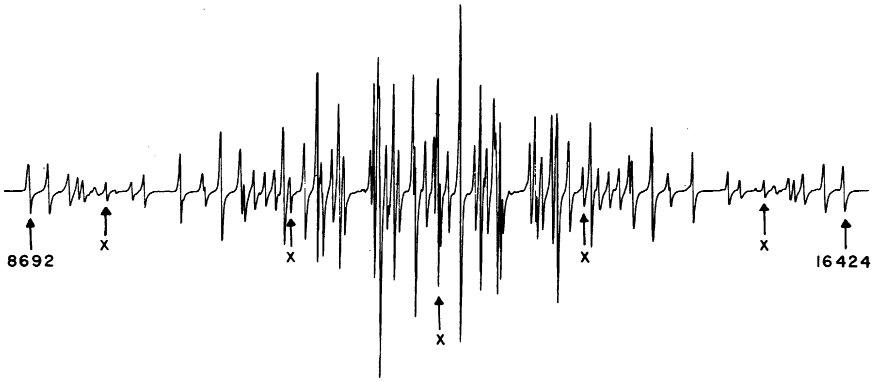

FIG. 3. EPR spectrum of a crystal of $CsCdBr_3$ doped with Gd^{3+}. The spectrum was recorded at room temperature with the field parallel to the crystallographic c axis. The frequency was 35.01 GHz. The resonances marked by **X** correspond to an isolated Gd^{3+} spectrum. The magnetic fields are given in gauss.

tant properties of the pair by analyzing the spectrum observed when the magnetic field is applied parallel to the principal axis of the Gd^{3+}-Gd^{3+} system.[8] Thus, it is necessary to include only the diagonal terms in the single-ion Hamiltonian. The charge-compensation-produced Gd^{3+}-Gd^{3+} pairs in the $CsMX_3$ crystals have an overall symmetry of D_{3h}; however, the symmetry at the Gd^{3+} ion site is C_{3v} (see Fig. 1). The threefold axis corresponds to the crystallographic c axis. The spin Hamiltonian for a Gd^{3+} ion in a C_{3v} site contains the following diagonal terms:

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

The crystal field operators O_n^0 are defined according to standard notation.[9] In our analysis the spin matrices were set up according to the procedure outlined by Hutchings, Birgeneau, and Wolf using the single-ion basis functions $|S_1, S_2, m_1, m_2\rangle$. The solutions to the total Hamiltonian were determined numerically by computer diagonalization of the spin matrices. The Hamiltonian parameters were varied until a satisfactory description of the observed pair spectrum was obtained. The parameters found by this procedure are reported in Table I.

The pair spectra exhibit an approximate symmetry about the center field (see Figs. 2 and 3). Each peak in the low-field portion of the spectrum has a corresponding peak in the high-field portion. Tables II–IV show a comparison of the observed and calculated shifts from the center field for the resonances from the Gd^{3+}-Gd^{3+} pairs in $CsMgCl_3$, $CsMgBr_3$, and $CsCdBr_3$. The overall fit in all three cases is quite good. Because of the large number of lines in the pair spectra it is possible to determine the magnetic interaction parameters J and α with a good deal of precision. A reasonably accurate estimate of the distance between the two Gd^{3+} ions in the pair can be obtained from the dipolar parameter α. If the two Gd^{3+} ions are treated as point dipoles, α can be calculated from the simple expression

$$\alpha = g^2\mu_B^2/R^3 ,$$

where R represents the separation between the two dipoles. Thus, the Gd^{3+}-Gd^{3+} separation can be computed directly from the experimentally determined α values. Table V shows the calculated Gd^{3+}-Gd^{3+} distances for the pairs in the three host lattices at room and liquid-nitrogen temperatures. The Gd^{3+}-Gd^{3+} separations are noticeably smaller than the distances between next-nearest-neighbor Mg^{2+} or Cd^{2+} ion sites in the host crystals. This observation is easily explained in terms of the structure of the Gd^{3+}-Gd^{3+} pair. Since the M^{2+} va-

TABLE I. Gd^{3+}-Gd^{3+} pair spin-Hamiltonian parameters. The number in parentheses is the estimated maximum error in the reported parameter.

Lattice	Temperature	g	J (cm^{-1})	α (cm^{-1})	b_2^0 (cm^{-1})	b_4^0 (cm^{-1})	b_6^0 (cm^{-1})
$CsCdBr_3$	Room	1.991 (1)	+0.000 68 (8)	+0.007 81 (8)	+0.042 33 (10)	+0.002 69 (5)	+0.000 17 (5)
	77°K	1.991 (1)	+0.000 59 (8)	+0.008 23 (8)	+0.043 94 (10)	+0.002 85 (5)	+0.000 19 (5)
$CsMgBr_3$	Room	1.991 (1)	+0.000 80 (8)	+0.008 41 (8)	+0.054 95 (10)	+0.002 64 (5)	+0.000 17 (5)
	77°K	1.991 (1)	+0.000 67 (8)	+0.008 71 (8)	+0.056 07 (10)	+0.002 82 (5)	+0.000 19 (5)
$CsMgCl_3$	Room	1.991 (1)	+0.001 07 (10)	+0.010 50 (10)	+0.045 08 (10)	+0.000 96 (5)	+0.000 09 (5)
	77°K	1.991 (1)	+0.001 16 (10)	+0.010 88 (10)	+0.046 62 (10)	+0.001 04 (5)	+0.000 09 (5)

TABLE II. Experimental and calculated line shifts (in gauss) for the Gd^{3+}-Gd^{3+} pairs in $CsMgCl_3$ at room temperature. ΔH_{expt} values were obtained by halving the difference between each resonance in the low-field half of the spectrum and the corresponding resonance in the high-field half; the spectrum was recorded at a frequency of 35.03 GHz.

ΔH_{expt}	ΔH_{calc}	Difference	ΔH_{expt}	ΔH_{calc}	Difference
7	5	+2	1851	1853	−2
250	248	+2	1899	1897	+2
258	258	−5	1948	1936	+12
	268		2023	2025	−2
385	381	+4	2150	2153	−3
426	426	0	2215	2219	−4
570	574	−4	2266	2267	−1
639	636	+3	2282	2289	−7
683	680	+3	2306	2312	−6
706	709	−3	2541	2543	−2
743	748	−5	2585	2574	+1
783	786	−3		2594	
850	853	−3	2754	2759	−5
1160	1158	+2	2804	2810	−6
1210	1212	−2	2954	2996	−42
1273	1261	+12	3206	3204	+2
1287	1277	+10	3243	3242	+1
1402	1404	−2	3375	3359	+4
1520	1519	+1		3371	
1536	1531	+2		3383	
	1537		3617	3614	+3
1576	1575	−3	3665	3662	+3
	1583		3846	3844	+2

TABLE III. Experimental and calculated line shifts (in gauss) for the Gd^{3+}-Gd^{3+} pairs in $CsMgBr_3$ at room temperature. ΔH_{expt} values were obtained by halving the difference between each resonance in the low-field half of the spectrum and the corresponding resonance in the high-field half; the spectrum was recorded at a frequency of 34.93 GHz.

ΔH_{expt}	ΔH_{calc}	Difference	ΔH_{expt}	ΔH_{calc}	Difference
159	161	−2	1905	1906	−1
211	202	+5	1991	1981	+10
	208		2147	2143	+4
343	342	−3	2297	2299	−2
	350		2366	2365	+1
375	373	+2	2449	2443	+1
519	518	+1		2452	
590	580	0	2643	2642	0
	589			2643	
	601		2796	2797	−2
826	826	0		2798	
941	942	−1	3174	3176	−2
1021	1022	−1	3536	3528	+8
1084	1084	−10	3698	3695	+3
	1105		4074	4067	+7
1292	1294	−2	4155	4159	−11
1358	1360	−2		4172	
1456	1455	0	4212	4213	−1
	1457		4339	4326	+8
1628	1628	0		4335	
1775	1773	+2	4522	4526	−4
1803	1804	−1	4707	4713	−6

TABLE IV. Experimental and calculated line shifts (in gauss) for the Gd^{3+}-Gd^{3+} pairs in $CsCdBr_3$ at room temperature. ΔH_{expt} values were obtained by halving the difference between each resonance in the low-field half of the spectrum and the corresponding resonance in the high-field half; the spectrum was recorded at a frequency of 35.01 GHz.

ΔH_{expt}	ΔH_{calc}	Difference	ΔH_{expt}	ΔH_{calc}	Difference
25	33	−8	1834	1829	+5
105	106	−1	1859	1853	−1
215	212	+3		1868	
222	222	0	2050	2051	−1
363	360	+3	2205	2202	+3
416	413	+3	2218	2220	−2
476	477	−1	2441	2441	0
598	595	+3	2781	2782	−1
621	624	−3	2898	2898	0
882	875	+8	3046	3056	−10
930	926	+4	3227	3227	0
933	939	−6	3356	3360	−5
993	995	−2		3363	
1093	1084	+2	3405	3405	0
	1099		3491	3488	−5
1142	1136	+4		3504	
	1139				
1255	1255	0	3685	3686	−3
1460	1458	+2		3690	
1541	1536	+5	3866	3867	−1
1635	1631	+4	4904	4897	+7
1738	1740	−2			

cancy located between the two Gd^{3+} ions (see Fig. 1) represents an excess of negative charge, it seems almost certain that the positively charged trivalent ions will be attracted toward this vacancy. This produces a Gd^{3+}-Gd^{3+} separation which is smaller than that predicted from the structure of the unperturbed host lattice. There is a small but measurable decrease in the calculated Gd^{3+}-Gd^{3+} distances when the doped crystals are cooled from room to liquid-nitrogen temperature. This decrease most likely results from the simple thermal contraction of the host lattice.

The Gd^{3+}-Gd^{3+} pairs in the $CsMX_3$ crystals do not seem to be particularly unusual when compared with other gadolinium pair systems. In all three host lattices the exchange interactions between the two Gd^{3+} ions are antiferromagnetic but extremely weak. The exchange parameters are more than an order of magnitude smaller in absolute value than any of those observed for nearest-neighbor and next-nearest-neighbor pairs in Gd^{3+}-doped crystals of $LaCl_3$ and $EuCl_3$.[8,10] The weakness of the exchange interactions in the $CsMX_3$ crystals presumably reflects the fact that Gd^{3+} ions are fairly far apart and are not connected by direct superexchange pathways. As might be expected, the

TABLE V. Calculated Gd^{3+}-Gd^{3+} separations and corresponding divalent ion separations in the unperturbed host lattice.

Lattice	Ion pair	Temperature	R (Å)
$CsCdBr_3$	Cd^{2+}-Cd^{2+}	Room	6.70
	Gd^{3+}-Gd^{3+}	Room	6.03
	Gd^{3+}-Gd^{3+}	77°K	5.93
$CsMgBr_3$	Mg^{2+}-Mg^{2+}	Room	6.50
	Gd^{3+}-Gd^{3+}	Room	5.89
	Gd^{3+}-Gd^{3+}	77°K	5.82
$CsMgCl_3$	Mg^{2+}-Mg^{2+}	Room	6.19
	Gd^{3+}-Gd^{3+}	Room	5.47
	Gd^{3+}-Gd^{3+}	77°K	5.40

exchange parameters appear to have an inverse dependence on the Gd^{3+}-Gd^{3+} separation. The exchange interaction is largest in $CsMgCl_3$ and smallest in $CsCdBr_3$.

It is clear from the intensities of the pair resonances that the vast majority (perhaps more than 90%) of the Gd^{3+} ions enter the $CsMX_3$ crystals as pairs. The extent to which the localized charge compensation requirement of the $CsMX_3$ lattice dominates the distribution of trivalent impurities is extraordinary. This effect is perhaps the most interesting aspect of these studies. The fact that the Gd^{3+} ions readily replace Mg^{2+} ions which are much smaller (0.66 vs 0.94 Å) indicates that the $CsMX_3$ crystals are rather accommodating host lattices. It would appear that within fairly broad limits the incorporation of impurities into these salts is determined solely by the electrostatics of the situation. This conclusion is supported by the observation that trivalent chromium, which is considerably different from gadolinium in size and chemical properties, also forms pairs when doped into the $CsMX_3$ crystals.[2,3] It seems likely that the $CsMX_3$ salts will prove to be extremely useful host materials for preparing and studying a variety of spectroscopically interesting pair systems.

ACKNOWLEDGMENT

The authors gratefully acknowledge Professor B.B. Garrett of Florida State University for the use of the E-12 spectrometer and helpful advice in recording spectra.

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