PHYSICAL REVIEW B VOLUME 18, NUMBER 11 1 DECEMBER 1978

Electron-paramagnetic-resonance spectrum of an exchange-coupled Cr^{3+}-Mo^{3+} pair

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(Received 28 June 1978)

When crystals of $CsMgCl_3$ are doped with Cr^{3+} and Mo^{3+} a significant concentration of an exchange-coupled Cr^{3+}-Mo^{3+} pair is produced. The electron-paramagnetic-resonance spectrum of the mixed pair is well described by a rather straightforward spin Hamiltonian. The exchange interaction is approximately 1.6 cm^{-1} and appears to be antiferromagnetic.

It has been known for some time that magnetically coupled "pairs" may be produced when paramagnetic impurities are introduced into diamagnetic crystals. Such pairs result when two paramagnetic impurities enter neighboring lattice sites in the host crystal. Electron-paramagnetic-resonance spectroscopy (EPR) is particularly effective in the identification and characterization of pair systems of this type. Although many EPR studies of coupled pairs appear in the literature, very few of these studies involve mixed pairs (pairs containing two different paramagnetic species). We have found that crystals of $CsMgCl_3$ which have been doped with Cr^{3+} and Mo^{3+} contain appreciable quantities of an exchange-coupled Cr^{3+}-Mo^{3+} pair. The EPR spectrum of the Cr^{3+}-Mo^{3+} pair is well described by a rather simple and straightforward spin Hamiltonian. This paper presents the results of our EPR characterization of this interesting and relatively unique magnetic system.

The host crystal $CsMgCl_3$ is one of a number of $CsMX_3$ salts which adopt the hexagonal $CsNiCl_3$ structure.[1] This structure can be described as an array of parallel linear chains composed of $MX_6{}^{4-}$ octahedra sharing opposite faces. The Cs^+ ions occupy positions between the linear chains. When trivalent ions are doped into crystals of this type there is a pronounced tendency for the impurity ions to cluster in pairs.[2–5] The pairs consist of two trivalent impurities associated with a divalent-ion vacancy. The stability of this particular arrangement arises from the rather strict charge compensation requirement of the $CsMX_3$ lattice. The combination of a vacancy with two trivalent ions provides a means by which trivalent impurities can be incorporated into a $CsMX_3$ crystal without disrupting the overall charge balance of the lattice. A schematic diagram of this charge compensation stabilized pair is shown in Fig. 1. Since the primary factors leading to pair formation are electrostatic rather than chemical, one would expect that a $CsMX_3$ crystal doped with two different trivalent ions would contain mixed as well as homogenous pairs. The EPR spectrum of $CsMgCl_3$ crystals doped with Cr^{3+} and Mo^{3+} indicates that this is the case (see Fig. 2). The features associated with the homogeneous pairs are easily identified by reference to the spectra of $CsMgCl_3$ crystals containing only Cr^{3+} or Mo^{3+}. The resonances marked by X in Fig. 2 are observed only when both Cr^{3+} and Mo^{3+} are present in the doped crystals. These resonances are assigned to the mixed Cr^{3+}-Mo^3 pairs.

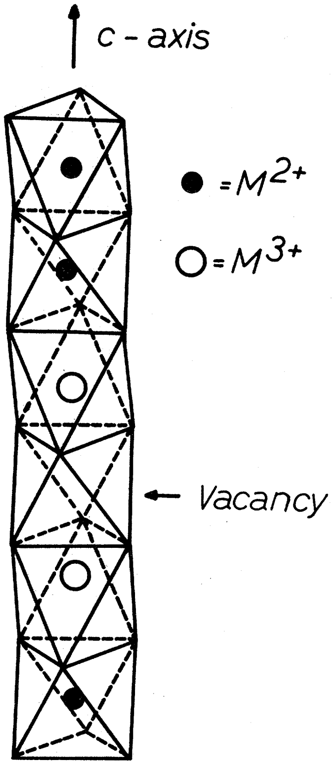

FIG. 1. Perspective drawing of a linear chain in the $CsNiCl_3$ structure showing the structure of the charge-compensated stabilized pair. The corners of the octahedra are occupied by halide ions.

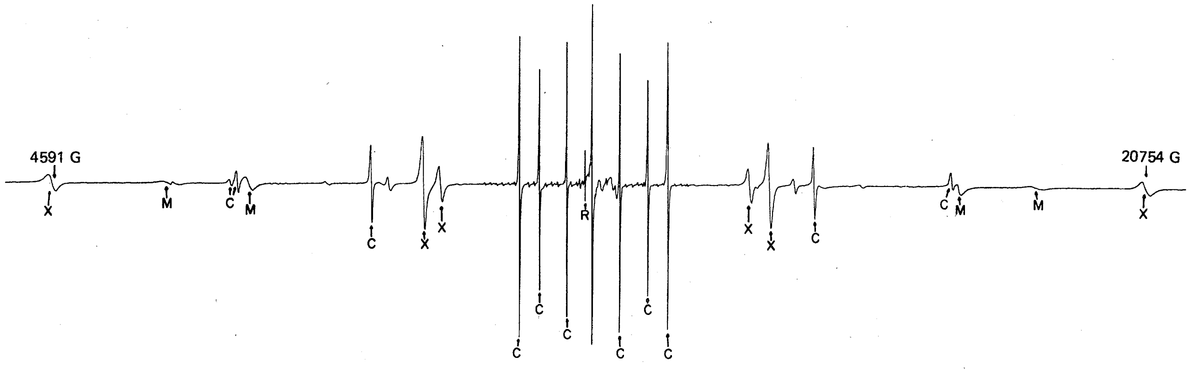

FIG. 2. Electron-paramagnetic-resonance spectrum of a CsMgCl$_3$ crystal doped with Cr^{3+} and Mo^{3+} recorded at 77 K with the magnetic field parallel to the crystallographic c axis. The frequency is 34.93 GHz. The resonances marked by C arise from Cr^{3+}-Cr^{3+} pairs, those by M from Mo^{3+}-Mo^{3+} pairs, and those by X from Cr^{3+}-Mo^{3+} pairs. The resonance labeled with R results from polycrystalline DPPH (α, α'-diphenyl-β-picryl hydrazyl) which is used as a frequency standard.

The spectra of the mixed as well as homogeneous pairs can be treated by a spin Hamiltonian of the following form:

$$H = H^P + H_1^S + H_2^S \ .$$

The magnetic interactions between the two ions are contained in H^P while the magnetic properties associated with each individual ion are included in H_1^S and H_2^S. Pair Hamiltonians of this type have been described in detail by Owen.[6,7] Since the pairs in CsMgCl$_3$ have axial symmetry, there are no rhombic terms in either the interaction or single-ion Hamiltonians. The interaction Hamiltonian allows both anisotropic and isotropic coupling:

$$H^P = J(\vec{S}_1 \cdot \vec{S}_2) + D_e(3\hat{S}_{1Z}\hat{S}_{2Z} - \vec{S}_1 \cdot \vec{S}_2) \ .$$

The single-ion Hamiltonian is standard for an axial $S = \frac{3}{2}$ system.

$$H^S = g_{\parallel}\mu_B H_Z \hat{S}_Z + g_{\perp}\mu_B (H_X \hat{S}_X + H_Y \hat{S}_Y) + D_c(\hat{S}_Z^2 - \tfrac{5}{4}) \ .$$

Application of the total Hamiltonian to the basis set of product spin functions for two $S = \frac{3}{2}$ ions ($|S_1 m_1\rangle |S_2 m_2\rangle$) gives a 16×16 energy matrix which can be solved by computer diagonalization. Since the treatment of homogeneous pairs is simplified by the fact that the single-ion parameters in H_1^S and H_2^S are identical, the Cr^{3+}-Cr^{3+} and Mo^{3+}-Mo^{3+} spectra were analyzed first. The adjustable parameters in the Hamiltonian were varied until the computer calculations gave satisfactory fits of the observed spectra. All of the important features of the Cr^{3+}-Cr^{3+} and Mo^{3+}-Mo^{3+} spectra including complete angular dependences are accurately reproduced by this treatment. The spectral analysis of the Cr^{3+}-Cr^{3+} and Mo^{3+}-Mo^{3+} pairs in CsMgCl$_3$ and other similar host crystals will be presented in detail elsewhere.[8]

The successful treatment of the homogeneous-pair spectra provides information which is very useful in the spectral analysis of the Cr^{3+}-Mo^{3+} pair. The single-ion properties, g values, and zero-field splittings of a paramagentic species are primarily determined by the immediate chemical environment. The two trivalent-ion sites in the charge-compensated stabilized pair are fairly well separated by the intervening vacancy. The immediate surroundings of a trivalent ion in

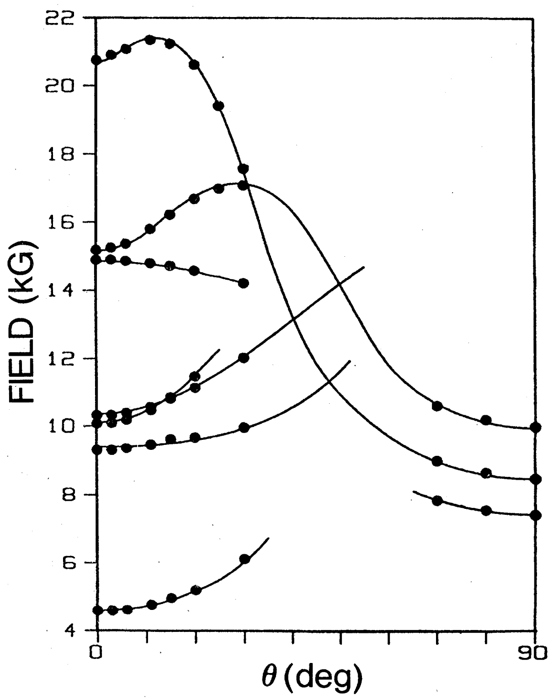

FIG. 3. Angular dependence of the Cr^{3+}-Mo^{3+} spectrum. The resonance fields are plotted vertically while the angles between the c axis and the magnetic field (θ) are plotted horizontally. The solid circles show the observed data while solid curves represent the calculated values.

TABLE I. Spin-Hamiltonian parameters of the coupled pairs in $CsMgCl_3$ at 77 K.

	Parameter	Cr^{3+}-Mo^{3+a}	Cr^{3+}-Cr^{3+b}	Mo^{3+}-Mo^{3+b}
H^P	J (cm^{-1})	+1.61	+0.96	+2.75
	D_e (cm^{-1})	+0.0029	−0.0081	−0.0033
H_1^S	$g_\parallel$	1.984	1.984	1.96
	$g_\perp$	1.985	1.985	1.96
	D_c (cm^{-1})	−0.222	−0.222	−1.14
H_2^S	$g_\parallel$	1.96		
	$g_\perp$	1.96		
	D_c (cm^{-1})	−1.14		

[a] In the mixed-pair Hamiltonian H_1^S and H_2^S are associated with Cr^{3+} and Mo^{3+}, respectively.

[b] For a homogeneous pair $H_1^S = H_2^S$.

one pair site should depend only slightly on the nature of the trivalent ion present in the second site. Thus, the single-ion properties of an ion in a pair system of this type should be nearly independent of the pair composition. Assuming that this is true, the parameters in the H_1^S and H_2^S terms of the Cr^{3+}-Mo^{3+} Hamiltonian can be taken directly from the analysis of the Cr^{3+}-Cr^{3+} and Mo^{3+}-Mo^{3+} pairs. This leaves only the interaction parameters J and D_e to be determined. With this approach a good fit of the mixed-pair spectrum is obtained from the computer calculations when suitable values for J and D_e are used. The agreement between the observed and calculated angular dependence of the Cr^{3+}-Mo^{3+} spectrum is shown in Fig. 3. Unfortunately, the angular variations of the resonances from the mixed pair are very difficult to follow at θ angles greater than 30° because of extensive overlap with resonances from the homogeneous pairs. (The angle between the principal axis of the pair, the crystallographic c axis, and the applied magnetic field corresponds to θ.) Although the experimental data do not cover the complete angular range, the excellent agreement between observed and calculated values indicates that the treatment of the mixed pair must be essentially correct. The spin-Hamiltonian parameters for the Cr^{3+}-Mo^{3+}, Cr^{3+}-Cr^{3+}, and Mo^{3+}-Mo^{3+} pairs in $CsMgCl_3$ are given in Table I. Only the relative signs of the parameters are unambiguously determined in this analysis. The choice of signs in Table I is based on the assumption that the anisotropic parameter D_e for the homogeneous pairs is dominated by the dipolar interactions. This requires D_e to be negative and implies that the isotropic exchange interactions are antiferromagnetic. In any case, it is clear that the sign of the isotropic exchange is the same in the mixed pair as in the homogeneous pairs. As might be expected the magnitude of the Cr^{3+}-Mo^{3+} interaction is intermediate between that of the Cr^{3+}-Cr^{3+} pair and that of the Mo^{3+}-Mo^{3+} pair.

It seems certain that the Cr^{3+}-Mo^{3+} pair is only one of a number of interesting exchange-coupled systems that can be prepared and characterized using the $CsMX_3$ salts as host crystals.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation under Grant No. CHE-77-12557.

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