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Electron Paramagnetic Resonance of Manganese(II) in $M_xMn_{1-x}Cl_2{\cdot}4H_2O$ ($M = Ni^{2+}$ and Co^{2+}): Exchange-Broadened Resonance Lines

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The EPR spectra of $Co_xMn_{1-x}Cl_2{\cdot}4H_2O$ with x in the range 0.00–0.31 have been obtained at room temperature and liquid nitrogen temperature. The line width is nearly independent of temperature and cobalt(II) admixture. On the other hand, the EPR spectra of $Ni_xMn_{1-x}Cl_2{\cdot}4H_2O$ with x in the range 0.00–0.61 reveal that the line width increases monotonically with increasing nickel(II) concentration. The phenomenological theory used to account for the variation of the Mn(II) line width with increasing Ni(II) concentration enables an order of magnitude estimate to be made of the Mn(II)–Ni(II) exchange interaction. The value obtained here is 3500 G which may be compared with the Mn(II)–Mn(II) value of 12 100 G. The lack of a line-width variation in the mixed-metal Mn(II)–Co(II) compound is associated with a particular phenomenological theory for a concentration dependence as well as the value of the spin–lattice relaxation time of the cobalt(II) ion.

Introduction and Theory

$MnCl_2{\cdot}4H_2O$ has been the subject of a wide variety of physical measurements including the EPR properties of both single crystals and polycrystalline samples.[1] The Lorentzian line shape, the temperature dependence, and the nearly isotropic nature of the single-crystal EPR line width (940 G peak to peak; $g = 2.00$) point to the dominance of three-dimensional spin–spin interactions, a result which also may be inferred from the crystal structure.[2] Earlier investigations at low temperature[3] also support this result.

The purpose of this paper is to report and to explain using a phenomenological theory the results of our EPR studies of the mixed-metal systems $Ni_xMn_{1-x}Cl_2{\cdot}4H_2O$ and $Co_xMn_{1-x}Cl_2{\cdot}4H_2O$, where x is the fraction of Ni(II) or Co(II) ion. Manganese chloride tetrahydrate forms an isomorphous series with nickel chloride tetrahydrate[4] and therefore is a suitable complex to study concentration effects as the Ni(II) ion is substituted for the Mn(II) ion in the lattice. In addition, we have found that the Co(II) ion can be incorporated into this lattice up to about 31% mole fraction of total metal content.

The phenomenological theory used to account for the variation of the Mn(II) EPR line width with Ni(II) concentration enables an order of magnitude estimate to be made of the Mn(II)–Ni(II) exchange interaction (H_e^1). An important aspect of this study is that this exchange interaction produces a broadening of the EPR lines with the addition of the Ni(II) ions rather than the more usual exchange narrowing.[5-7] The dipolar interaction invariably leads to EPR line broadening whereas the isotropic exchange interaction can result in either narrowing or broadening. For exchange broadening to occur, the interacting spins must have sufficiently different g values which give rise to two distinct resonance lines whose separation is large compared with their widths. This implies that the spin–spin interaction between these unlike spins is small compared with the difference in their Zeeman energies. Van Vleck and others[5-7] have shown that under these conditions the exchange interaction does not commute with the total magnetic moment resulting in an increased second moment and an "exchange-broadening" resonance curve.

The Co(II) ions were introduced into the $MnCl_2{\cdot}4H_2O$ lattice in order to study the effects of magnetic dilution. Such dilution can be obtained by incorporating diamagnetic ions into a host lattice or by using paramagnetic ions whose spin–lattice relaxation time is much shorter than the Larmor precession period of the resonating paramagnetic ion in the temperature range of interest.[8-11] This condition is expected to be fulfilled for the Co(II) in the distorted octahedral geometry surrounding the metal ion in this lattice.[7] A brief description of some aspects of the effects of the Co(II) ion has been reported previously.[12]

Table I. EPR Line Width (Half-Width at Half-Maximum of the Absorption Curve) for Mn(II) in $M_xMn_{1-x}Cl_2{\cdot}4H_2O$ as a Function of Composition and Temperature

		line width G	
x^a	% water	298 K	77 K
	M = Co(II)		
0.00	36.4	814	792
0.03	35.6	785	826
0.11	36.1	823	806
0.19	36.4	806	875
0.81	37.2	806	869
	M = Ni(II)		
0.00	36.4	814	792
0.04	36.8	844	869
0.12	36.0	927	944
0.27	38.3	1031	1047
0.37	35.5	1151	1252
0.61	35.7	1503	1539

[a] Mole fraction of total metal content.

Sample Preparation and Experimental Measurements

Polycrystalline samples of Ni(II)- and Co(II)-doped $MnCl_2{\cdot}4H_2O$ were prepared by slow evaporation of aqueous solutions at room temperature. The water content of the crystals was determined by thermogravimetric analysis. The analyses were all within 1% of the 36.4% expected for the pure material (Table I). X-ray powder patterns of the doped material were virtually identical with those of $MnCl_2{\cdot}4H_2O$. Concentrations of the metal ions were determined by atomic absorption spectrophotometry.

EPR data were obtained on a Varian V-4500 EPR spectrometer and the magnetic field was monitored with a NMR gaussmeter. The line widths at 298 and 77 K for the samples studied are listed in Table I. There was no evidence for a "half-field" resonance line associated with the Ni(II) resonances. Although such absorptions could be present, they may be too broad to be observed.

Results and Discussion

Co(II) Doping. Mn(II) EPR line widths at 298 and 77 K are listed as a function of Co(II) ion concentration in Table I. At room temperature the Co(II) ion has no effect on the Mn(II) EPR line width. At 77 K there appears to be a slight broadening, a result consistent with other observations.[13-15] This latter result should be regarded with some caution because of the uncertainty (about 8%) in the experimental data. Thus, it appears that the effect of Co(II)–Mn(II) exchange is minimal at room temperature but that this exchange may be contributing to the slight increase in line width with Co(II)

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concentration observed at liquid nitrogen temperature.[13]

Co(II) behaves as a diamagnetic diluent in the manganese(II)–cobalt(II) chloride tetrahydrate system. Because of the short spin–lattice relaxation time of Co(II), its resonance line is too broad to be observed. This same short spin–lattice relaxation time induces rapid motion of the Co(II) spin system which precesses at a different frequency from that of the Mn(II) ion. Thus the Mn(II) resonance line is well separated from any Co(II) resonance effects, and the Mn(II) ion acts as if it were in a nonmagnetic crystal. A similar result was noted by Date,[14] Ono and Hayashi,[11] and others,[10-15] who have studied extensively the effects of the Co(II) ion on Mn(II) ions doped into cobalt Tutton salts.

The exchange-narrowed EPR line width may be formulated in a simple way to indicate the variation of the concentration. The expression is

$$H(x) = \frac{10}{3}\,\frac{1 - x}{(1 - x)^n}\,\frac{(H_d(0))^2}{H_{ex}(0)} \tag{1}$$

where x is the concentration of the diluting metal ion (Co(II) in this case), $H_d(0)$ is the dipolar width for the nondiluted system Mn(II), $H_{ex}(0)$ is the corresponding exchange field, and n is a number expected to be between 0.5 and 1.[16-20] The $^{10}/_3$ factor arises from the observation field being much less than the expected exchange field. The concentration dependence for the dipolar term is known to vary as $(1 - x)\cdot(H_d(0))^2$.[17-20] The lack of a strong concentration dependence to the line width in this case suggests $n \approx 1$. The dipolar field is estimated from the Van Vleck formula for an isotropic distribution of magnetic ions and found to be $H_d(0) = 1720$ G. From this and the average line width at room temperature we find $H_{ex}(0) = 12.1$ kG.[1] There is an order of magnitude agreement between this result and low-temperature susceptibility calculations.[3] Moreover, the Q-band EPR data of Servant and Palangie[21] and the ratio method[22] for determining H_{ex} also produce similar values.

Ni(II) Doping. The d^5 configuration of the Mn(II) ion is spherically symmetric and not strongly coupled to the lattice. Hence, its g value is close to the free-electron value of 2.00. On the other hand, the Ni(II) ion's d^8 configuration is not spherically symmetric resulting in a g value that is typically about 2.25.[3] As the Ni(II) ions could have strong spin–spin interactions with the Mn(II) ions, we might expect a change in line width and a significant g shift with doping.

The Mn(II) g values for all Mn–Ni complexes were found to be independent of both temperature and Ni(II) ion concentration and lie close to 2.00, the g value of $MnCl\cdot4H_2O$. However, we estimate that the uncertainty in g resulting from the very broad resonances could be as large as 0.04.[23]

Table I lists the variation of the Mn(II) EPR line width at 298 and 77 K as the Ni(II) ion concentration is increased. The increase in line width is approximately linear with no significant difference between the data at the two temperatures. The lack of an appreciable temperature dependence suggests no significant spin–lattice interaction effects.

For the line broadening to occur without Mn(II)–Ni(II) exchange the result would have to be the result of the dipolar interaction. This is unlikely since Van Vleck has shown that dipolar interactions between dissimilar ions are only $^4/_9$ as effective as those between similar ions in broadening an EPR line. The greater effectiveness of the dipolar interaction with like atoms has its physical basis in these atoms participating in the same resonance. The same effect shows up mathematically in the irrelevance of more terms in the Hamiltonian since the resonances produced by such terms are well separated from the resonance of interest if the atoms are unlike.

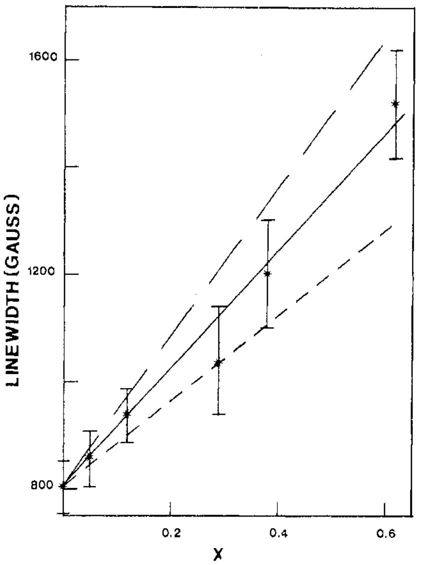

Figure 1. Graph of half-width at half-maximum of Mn(II) EPR absorption signal in manganese(II)–nickel(II) chloride tetrahydrate vs. x (mole fraction of Ni(II)): (---) calculated for $H_{ex}{}^1 = 3000$ G, (—) calculated for $H_{ex}{}^1 = 3500$ G, (– – –) calculated for $H_{ex}{}^1 = 4000$ G. Experimental points are an average value of the 298 and 77 K data.

On the other hand, large exchange interactions between unlike spins ($H_e{}^1 \ll H_{ex}$) would pull the two resonance curves together into a single curve located at an intermediate g value. In this case exchange narrowing is expected and a significant g-factor shift to higher values would occur, particularly at high Ni(II) concentrations.[24] Since the experimental uncertainty in the g-value shift is larger at the higher Ni(II) concentration, this aspect cannot, by itself, be used to rule out the case of strong exchange, but the lack of exchange narrowing can justify this conclusion. Thus, the exchange broadening must result from an intermediate exchange interaction ($H_{ex} \simeq H_e{}^1$) between dissimilar ions.

For the $Ni^{II}Mn^{II}Cl_2\cdot4H_2O$ system the EPR line-broadening terms are expected to be (1) the Mn–Mn dipolar interaction, H_d, (2) the Mn–Ni dipolar term, $H_d{}^1$, and (3) the Mn–Ni exchange term, $H_e{}^1$. The only line-narrowing term expected is the Mn–Mn isotropic exchange term, H_{ex}. Other terms such as those which arise from Mn(II)–Mn(II) antisymmetric exchange and anisotropic exchange have been excluded from this model for reasons to be discussed below.

Thus, the Mn(II) EPR line width is expected to vary approximately as

$$\Delta H(x) = [{}^{10}/_3(1 - x)(H_d(0))^2 + {}^4/_9(x(1 - x))^{1/2}(H_d{}^1(0))^2 + f(x)(H_e{}^1)^2]/[(1 - x)H_{ex}(0)]$$

where x and $1 - x$ are the fractions of Ni(II) and Mn(II) ions, respectively. Again the $^{10}/_3$ factor appears in the Mn(II)–Mn(II) dipolar interaction because the experiments were all carried out at X-band frequencies which should be in the region where $H_0 \ll H_{ex}$. The reason for the $^4/_9$ factor in the Mn(II)–Ni(II) dipolar interaction has already been explained. The dipolar interaction, $H_d{}^1(0)$, again was estimated from the Van Vleck formula with an average spin used for the mixed system. Perhaps a frequency (or field) dependent factor should have been used on this term since $H_e{}^1 \approx H_0$ (vide infra), but this would not alter the conclusions since this term is much smaller than the effects of the Mn(II)–Ni(II) exchange (third term).

The concentration dependence for the Mn(II)–Mn(II) dipolar term and the corresponding exchange term have been discussed previously. The concentration dependences for the Mn(II)–Ni(II) terms are extensions of these and $f(x)$ is taken to be $x(1 - x)$. This is consistent with the linear concentration dependence since the Mn(II)–Ni(II) dipolar term is too small to produce the observed increase in line width.

The only free parameter is H_e^1, all others having been previously fixed or calculated. A value of $H_e^1 = 3500$ G produces the best fit to the observed data (Figure 1).

This value of an exchange field is consistent with the assumption that the system is in the intermediate exchange range. Since the anisotropic and antisymmetric exchange line-broadening terms[24,25] are expected to vary as $(\Delta g/g)^4 H_{\rm ex}$[12] and $(\Delta g/g)^2 H_{\rm ex}$,[12] respectively, and $\Delta g/g \simeq 0.1$, these terms are clearly smaller than H_e^2 itself. This provides the justification for considering only the isotropic exchange terms in the line-broadening expression.

Finally it should be emphasized that the treatment of these data is based on several simplifying assumptions. Most notably these are (1) a simple form for the line-width dependence for the Mn(II)–Mn(II) interaction and (2) the use of the $^{10}/_3$ factor over the full concentration range, which may not be applicable. Thus the value of H_e^1 should be regarded as an order of magnitude estimate of the Mn(II)–Ni(II) isotropic exchange interaction at room temperature.

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Ligand Field Photochemistry of *cis*-α- and *cis*-β-Triethylenetetramine Complexes of Rhodium(III)

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The photosensitivity of *cis*-α- and *cis*-β-$[Rh(trien)ClX]^{n+}$ (X = Cl, H_2O) toward chloride loss and isomerization is dependent upon the geometric configuration of the trien ligand. *cis*-α- and *cis*-β-$[Rh(trien)Cl(H_2O)]^{2+}$ and *cis*-α-$[Rh(trien)Cl_2]^+$ give *trans*-$[Rh(trien)Cl(H_2O)]^{2+}$ as the sole photoproduct, while *cis*-β-$[Rh(trien)Cl_2]^+$ yields a mixture of 65% *cis*-β- and 35% *trans*-$[Rh(trien)Cl(H_2O)]^{2+}$ as primary photoproducts. The cis-β ions undergo aquation/isomerization at quantum efficiencies ($\phi \approx 0.4$) typical of chloride labilization from less chelated haloamine complexes of Rh(III), and the cis-α ions are at least 2 orders of magnitude less photoreactive than the isomeric cis-β ions. A model, involving excited-state distortion toward a trigonal-bipyramid (TBP) geometry, is proposed to account for the photoinduced isomerizations at efficiencies dependent upon the ground-state geometry.

Introduction

Ligand field irradiation of Rh(III) complexes in aqueous solution typically leads to efficient ligand substitution (aquation) with no measurable interference from redox processes.[1] The semiempirical and theoretical models used to describe the ligand field photochemistry of Cr(III)[2] and Co(III)[3] have been extended to Rh(III)[4] complexes, but with limited success.[5] Theoretical analysis of Rh(III) photochemistry is complicated by an inner-system crossing, as low-lying triplet states have been identified as the photoreactive states in the halopentaammine rhodium(III) cations.[6] The interpretation is further hampered by the stereochemical consequences of ligand field irradiation.

The available studies reveal a tantalizing mixture of stereoretention and stereomobility upon ligand field irradiation of Rh(III) complexes; models have not yet been presented which account for this seemingly inconsistent behavior. Stereoretentive aquation of the low-field ligand appears to be the norm for trans-disubstituted tetramine complexes of Rh(III),[7a] in contrast to the stereomobility observed for several cis-disubstituted tetramines. Photolysis of *cis*-$[Rh(NH_3)_4Cl_2]^+$[8] and *cis*-$[Rh(en)_2Cl_2]^+$[7b] leads to the corresponding *cis*-chloroaquo ions, while photolysis of *cis*-$[Rh(cyclam)Cl_2]^+$[9,10] at "natural pH" in H_2O/CH_3CN solution

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