The Electronic Spectrum of Chromium(II) in a Diamagnetic and a Paramagnetic Layer Lattice Host

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Abstract

Cr^{2+} ions can be doped into an $MgCl_2$ layer lattice up to about an 18% replacement of Mg^{2+} with Cr^{2+}. Electronic spectra show no evidence of Jahn–Teller distortion and indicate that the chromium site is centrosymmetric. Thus, the Cr^{2+} geometry is defined by the lattice. Both Mn^{2+} and Cr^{2+} nearest neighbours enhance the intensity of spin forbidden bands and Cr^{2+} in a paramagnetic $MnCl_2$ host lattice shows a similar effect. Comparison with other systems suggests that the mechanism of exchange is dependent on the electronic structure of the neighbouring ions.

Introduction

The electronic structure of divalent ions of the transition metals titanium, vanadium and chromium have received less attention than their counterparts from the right-hand side of the first transition row partly because many of their compounds are relatively easily oxidised both in solution and in the solid state. However, at between 600 and 900 °C in a halide melt these oxidation states are quite stable and consequently by growing crystals from these melts it is possible to trap the ion in a suitable host in a solid solution. As part of a study of the electronic spectra of these ions, a series of crystals was prepared in which anhydrous $CrCl_2$ was doped into $MgCl_2$ and $MnCl_2$. Both $MgCl_2$ and $MnCl_2$ are layer lattices with the metal ion occupying every second layer of octahedral vacancies between layers of chloride ions. In our studies we have used a diamagnetic host lattice ($MgCl_2$) so that chromium–chromium and chromium–manganese pair interactions can be studied and a paramagnetic host lattice ($MnCl_2$) so that the effect of a cluster of neighbouring paramagnetic ions on the chromium impurity site can be studied.

Since chromium(II) is a d^4 system with one electron in its eg set of orbitals, spectra of this ion often

indicate a Jahn–Teller distortion. For example, in the spectrum of single crystal $CrCl_2$ [1] the spin allowed band in the near infrared is split into three components. This distortion is also evident in the spectra of CrF_2 [2,3], in more complex halides of general formulae $MCrX_3$ and M_2CrX_4 [2,4], and in the dihydrates $M_2CrX_4 \cdot 2H_2O$ [5] (M = univalent cation and X = a halide anion). The degree of such distortion is dependent on the environment occupied by the Cr^{2+} ion and studies of linear chain systems of the type $ACrX_3$ [6–8] show that the spin allowed transition exhibits no appreciable splitting. Thus, one question which we wished to investigate was whether the chromium ion would direct its local environment and appear in Jahn–Teller distorted form or whether the lattice stability would be such that an octahedral chromium site would result.

The spin forbidden quintet to triplet transitions of Cr^{2+} can be observed in pure chromium II compounds and in some doped systems [2–8]. Transitions to triplet free ion terms can be resolved into 18 identifiable states in a field of D_{4h} symmetry. The energy region between 15 000 and 20 000 cm^{-1} is particularly complex [9] but, as we shall show, the bands in this region can be assigned on the basis of previous studies. The results indicate the importance of these relatively covalent lattices in determining both the ion site geometry and the relative intensities of the spin forbidden bands and this latter point is discussed in terms of a simple spin exchange model which can be adapted to take account of clusters of paramagnetic ions as well as pairs.

Experimental

Anhydrous $CrCl_2$ was prepared by melting stoichiometric amounts of chromium powder (Johnson Matthey) and anhydrous zinc chloride (Analar) in an evacuated silica ampoule at 900 °C for 48 h. The ampoule was cracked open in a glove box with a dried argon atmosphere. This yielded a small quantity of pure $CrCl_2$ crystals which were used for doping into the host lattice. The ampoule also yielded a larger amount of $CrCl_2$ contaminated with zinc

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metal and a plug of zinc metal at the bottom of the ampoule.

Anhydrous magnesium chloride and manganese chloride were prepared by a similar method using magnesium powder or manganese powder in place of the chromium powder. In both cases the yield of product was in excess of 95%.

Each of the crystals was grown by the Bridgeman method. The required amount of each material was loaded into a 12 mm OD silica tube which had been heated with a gas torch for 10 min on a vacuum line to remove any surface hydroxyl groups. The tubes were then sealed on a vacuum line and lowered through a furnace with a hot section at 850 °C at a rate of 2 in/day. On removal from the furnace the tubes were opened in a glove box to reveal a boule of single crystal product.

Both host lattices cleaved easily perpendicular to the *c*-axis but it proved impossible to produce samples with faces parallel to the *c*-axis. Consequently polarised data do not form part of this study.

For the low doped $Cr^{2+}/MgCl_2$ and for $Cr^{2+}/Mn^{2+}MgCl_2$, prepared samples were approximately 5 mm × 5 mm and for high doped $Cr^{2+}/MgCl_2$ and $Cr^{2+}/MnCl_2$ they were about 4 mm × 3 mm. All samples were hydroscopic and sample preparation was carried out in a portable glove box flushed constantly with dry, oxygen free nitrogen. All samples had their optical faces polished using Diamix paste on a glass plate. The thickness of each sample was measured with a micrometer before it was mounted in the cryostat and after all spectra had been recorded a sample of the crystal was used to determine Cr^{2+} concentration by atomic absorption spectroscopy. Using this measurement it is possible to calculate molar absorptivities.

The crystals were mounted on a copper foil with a 2 × 2 mm aperture. The foil was attached by Crycon heat conducting grease to the cold finger of an Air Products Displex closed cycle cooling unit. Spectra were recorded with a Beckmann Acta IV IR/UV–Vis spectrometer. This machine had IR optics modified to optimise sensitivity in the range 800–2000 nm.

Results and Discussion

Magnesium and manganese chlorides crystallize with the cadmium iodide structure. This structure consists of layers of chloride ions with the metal ions occupying octahedral holes in every second layer. In any one layer the line of centres between a pair of metals runs between two chloride ions which are in contact and consequently in plane exchange effects between the metals occur mainly by superexchange involving orbitals from the intervening halide ions. The distances between the metal ions between layers

is longer but in fact there is no intervening chloride and a different weaker type of exchange occurs. Manganese chloride has a Neel point of 2.3 K and consequently long range magnetic ordering in the host lattice is unlikely to be observed in the spectra down to the base temperature in this study of 10 K. Thus, with the paramagnetic manganese chloride host lattice any exchange effects are best considered as due to a local cluster of a chromium ion with six surrounding manganese ions in the same plane.

1.75% $Cr^{2+}/MgCl_2$

The lowest doped sample of chromium in magnesium chloride gives an electronic spectrum which contained only one d–d band due to the spin allowed $^5E_g \rightarrow ^5T_{2g}$ transition (Fig. 1). There is no evidence of a Jahn–Teller distortion and consequently it would appear that the geometry of the ion is constrained by the surrounding $MgCl_2$ lattice. At 293 K, the band has a 10 Dq value of 10 000 cm^{-1}. On cooling it shifts to a higher energy (10 640 cm^{-1}) and there is a decrease of about 30% in oscillator strength. This behaviour is characteristic of a transition metal ion in a centrosymmetric environment and consequently supports the conclusion that the Cr^{2+} environment is not Jahn–Teller distorted.

Even at this low level of doping some chromium–chromium pair formation might have been expected, particularly if complete solid solution had not been achieved and in a study of $Cr^{2+}/CsMgCl_3$ [6] with a doping level of 6.4% Cr^{2+}, exchange induced quintet to triplet transitions have been observed. The UV–Vis spectrum of this sample however has no such structure and it would appear that the chromium ions are isolated.

18% $Cr^{2+}/MgCl_2$

The $^5E_g \rightarrow ^5T_{2g}$ transition in a sample with 18% magnesium ions replaced by chromium is at a higher energy than with the lower chromium concentration but the same decrease in oscillator strength on cooling is observed (Fig. 2). However the shape of the band at 293 K is different from that in the lower doped sample. It would appear that this is due to
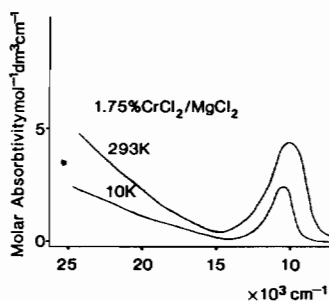

Fig. 1. Spectrum of the $^5E_g \rightarrow ^5T_{2g}$ spin allowed band of Cr^{2+} from a sample of Cr^{2+} in $MgCl_2$ at a low level of doping.
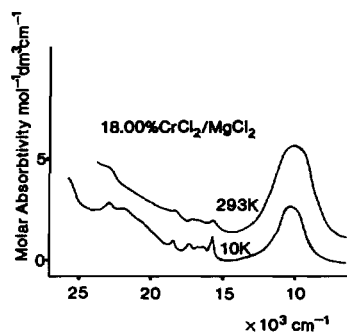
Fig. 2. Spectrum of Cr^{2+} from a $Cr^{2+}/MgCl_2$ sample at a high level of doping.

Fig. 3. Spin forbidden Cr^{2+} bands. For assignments 1-6 see text.

strain in the crystal causing some unresolved splitting of the band, although a fairly symmetric environment is still indicated by the temperature dependence. It proved difficult to grow crystals at higher concentrations and although one crystal was made and evidence of a Jahn—Teller distortion observed, this experiment could not be repeated and it was in general the case that compounds with greater concentrations of chromium could not be made as good single crystals. Thus, it may be that at higher concentrations the effect of distortion by chromium ions leads to a disruption of the magnesium chloride layer lattice system. Chromium chloride differs from the other first row dihalides apart from copper in that it does not itself have a layer lattice structure and consequently although very high concentrations of dopant have been obtained when both cations form a layer lattice as pure halides, the change in structure in the present case may explain why we could not obtain greater amounts of chromium in magnesium chloride. At about 18% chromium replacement of magnesium, the beginning of a change from a layer lattice is seen in the change in shape of the spin allowed band on cooling. At low temperatures the band at 10 K most closely resembles that found for the low doped samples suggesting that loss of thermal energy on cooling constrains the geometry of the Cr^{2+} ion more effectively into the high symmetry host lattice configuration.

The near IR and visible region of the spectrum show considerable structure due to spin forbidden transitions (Fig. 3). There are five main bands at 15 924 cm^{-1} (1), 16 526 cm^{-1} (2), 17 668 cm^{-1} (3), 18 727 cm^{-1} (4) and 23 255 cm^{-1} (6). In addition there is a large, broad absorption centred at 22 400 cm^{-1} (5). The ligand field energy diagram [9] for a d^4 ion shows no quintet to triplet transition corresponding to the energy of band (5) for a Dq value of 10 645 cm^{-1}. However the transition is at approximately double the energy of the $^5E_g \rightarrow {}^5T_{2g}$ transition and is assigned as a double excitation of the $^5E_g \rightarrow {}^5T_{2g}$ transition using two exchange coupled Cr^{2+} ions. This is the same assignment as given by

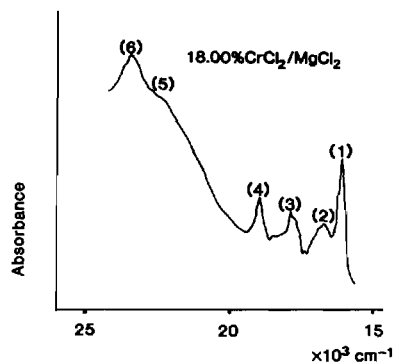McPherson *et al.* to a transition at 20 000 cm^{-1} for $Cr^{2+}/CsMgCl_3$ which has a Dq value of 1145 cm^{-1} [6]. The five other bands are assigned to quintet $\rightarrow$ triplet transitions. Oelkrug [2] has identified five such transitions in the region between 15 000 and 20 000 cm^{-1} and although this treatment ignores spin orbit coupling as employed by Konig and Kremer [9] the assignments are similar. For octahedral symmetry the order of levels in this region is $^3E_g(^3H) < {}^3T_{1g}(^3H) < {}^3T_{2g}(^3H) < {}^3A_{1g}(^3G) < {}^3A_{2g}(^3F)$. The three lowest energy transitions are assigned as follows:

(1) 15 924 cm^{-1} $^5E_g \longrightarrow {}^3E_g(^3H)$

(2) 16 529 cm^{-1} $^5E_g \longrightarrow {}^3T_{1g}(^3H)$

(3) 17 668 cm^{-1} $^5E_g \longrightarrow {}^3T_{2g}(^3H)$

Transition (d) lies in a region where both $^3A_{1g}(^3G)$ and $^3A_{2g}(^3F)$ excited states are possible. By comparison with other work this transition is assigned as $^5E_g \rightarrow {}^3A_{1g}(^3G)$ with transition (6) assigned as $^5E_g \rightarrow {}^3E_g(^3G)$ [4–6].

5.66% Cr^{2+}/MnCl$_2$

The shape, energy and temperature dependence of the Cr^{2+} spin allowed band in $Cr^{2+}/MnCl_2$ is similar to the Cr^{2+} spin allowed band in 1.75% $Cr^{2+}/MgCl_2$ (Fig. 4). It gives a 10 Dq value of 10 000 cm^{-1} at 293 K, increasing to 10 640 cm^{-1} at 10 K and there is a decrease in oscillator strength as the temperature is lowered. The paramagnetic matrix however might be expected to enhance the intensity of formally spin forbidden bands but the spectra of $MnCl_2$ covers the area where most of these bands would be expected to occur and as a consequence only the lowest energy spin forbidden Cr^{2+} transitions can be observed. Figure 5 shows the spectrum below the lowest energy Mn^{2+} transition at 10 K. There are two main bands centred on 15 898 cm^{-1} (1) and 16 835 cm^{-1} (2). Because of the similar values of Dq for Cr^{2+} in manganese and magnesium chlorides, assignments of
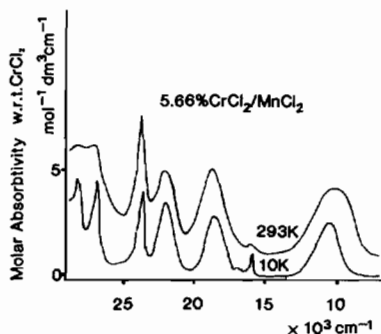
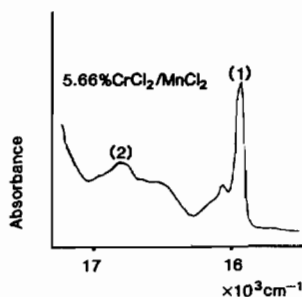Fig. 4. Spectrum of Cr^{2+} in a paramagnetic $MnCl_2$ layer lattice.

Fig. 5. Spin forbidden Cr^{2+} bands in the $MnCl_2$ lattice.

Fig. 6. Spectrum from a crystal of $MgCl_2$ doped with both Cr^{2+} and Mn^{2+}.

Fig. 7. Full structure of the $^5E_g \rightarrow {^3}E_g(^3H)$ transition of Cr^{2+} from a crystal of $MgCl_2$ doped with both Cr^{2+} and Mn^{2+}.

these bands follow from the $Cr^{2+}/MgCl^{2+}$ analysis. Transition (1) is assigned as $^5E_g \rightarrow {^3}E_g(^3H)$ and (2) as $^5E_g \rightarrow {^3}E_g(^3H)$. Associated with band (1) is a weak side band centred on $16\,038$ cm^{-1}, which appears to be a component of the $^5E_g \rightarrow {^3}E_g(^3H)$ transition. Transition (2) has no equivalent transition in magnesium chloride but the low energy shoulder at $16\,529$ cm^{-1} corresponds to the band $^5E_g \rightarrow {^3}T_{2g}(^3H)$ and it maybe that the additional, more intense structure is due either to magnon assisted sidebands or vibronic structure.

4.5% Cr^{2+} 4.46% $Mn^{2+}/MgCl_2$

The spectrum from a sample of magnesium chloride double doped with Cr^{2+} and Mn^{2+} is dominated, as would be expected, by the Cr^{2+} spectrum (Fig. 6). The behaviour of the spin allowed chromium band is rather similar to that for the 1.75% Cr^{2+} sample but there is evidence of selective enhancement of the $^5E_g \rightarrow {^3}E_g(^3H)$ spin forbidden transition of Cr^{2+} by the neighbouring Mn^{2+} ions. It can be resolved at 10 K to give some fine structure (Fig. 7) which appears to consist of two components split by about 30 cm^{-1} and a vibrational progression based on one of them which has a period of 41 cm^{-1}. A progression interval as low as this is likely to be due to coupling with a lattice mode of the system.

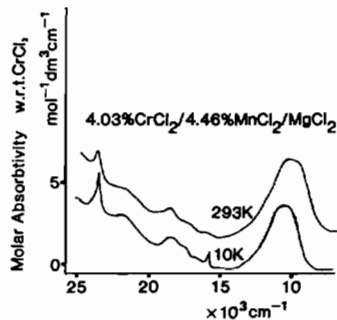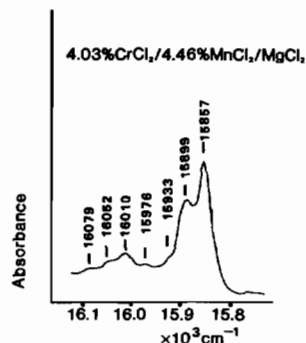Electronic spectra in which some intensity is due to exchange between neighbouring paramagnetic ions have been investigated for paramagnetic salts [10–13], ion doped crystals [14–19], and polymetallic molecular species [20, 21]. Conceptually the simplest model is that in which two neighbouring paramagnetic ions couple through bridging halides to form an exchange coupled dimer. Using the spin only approach a manifold of spin states such that $S_T = (S_a + S_b) \rightarrow (S_a - S_b)$ would be expected. For d^4 in the ground state, a manifold of spin states of $S_T = 4,3,2,1,0$ is obtained and for a triplet excited state a manifold of spin states of $S_T = 3,2,1$ is obtained. In pure $CrCl_2$, in plane Cr^{2+} ions are coupled ferromagnetically and we assume that the $S_T = 4$ state is the lowest level of the ground state in this case (Fig. 8). However there is no strong evidence for this and the argument we use will work equally well for antiferromagnetic coupling.

With titanium(II), hot bands appear in the spectra at higher temperatures [22] but in this case none is observed and the change in oscillator strength with temperature can be accounted for by thermal broadening and reduced exchange coupling between cations caused by the effect of thermal energy. The spectra of the $^5E_g \rightarrow {^3}E_g(^3H)$ for $Cr^{2+}/MnCl_2$ illustrates this point but it is true of the other crystals studied as well (Fig. 9). This absence of hot bands could be due to a number of factors such as a greater separation between excited state levels than ground state levels, or very large or small separations between ground
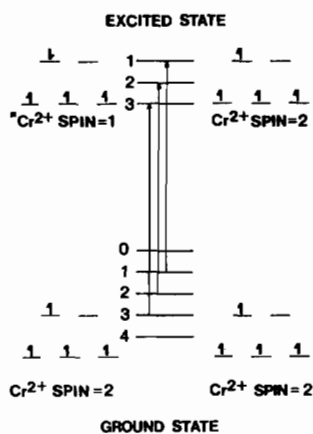
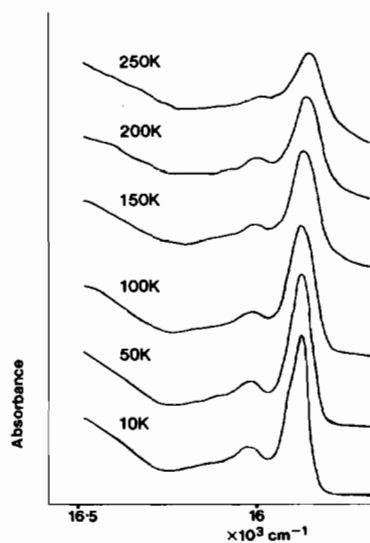Fig. 8. Exchange coupling of two Cr^{2+} ions showing individual spin states obtained using a spin only approach.

Fig. 9. Temperature dependence of the $^5Eg \rightarrow Eg(H)$ transition from a sample of Cr^{2+} in $MnCl_2$.

intensity of spin forbidden band systems. This is in contrast to titanium where titanium interactions do not give rise to the increased intensity of titanium spin forbidden bands [23, 24] but titanium—manganese interactions do. The greater variety of interactions possible with eg as well at t_{2g} orbitals occupied may be a prerequisite for an exchange effect of this type and may also give rise to smaller individual splittings between spin states.

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state levels. The most apposite explanation which best fits the temperature dependence observed is that the splitting in chromium is between 10 and 20 cm^{-1} in the ground state compared to about 40 to 50 cm^{-1} in titanium and hence splitting, other than the partial resolution of a shoulder (15 899 cm^{-1} in Fig. 7), will not be observed.

Thus, exchange between chromium and either chromium or manganese neighbours give rise to added