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Effect of Titanium–Titanium Interactions on the Electronic Spectrum of Titanium(II) Ions in the Layer Lattice $MgCl_2$

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The electronic spectrum from titanium(II) ions doped into a magnesium chloride host lattice is reported for four different titanium ion concentrations. At the lowest concentration (a Ti to Mg atomic ratio of 1/100), the spectrum is that expected for an isolated titanium(II) ion in a centrosymmetric environment. As the concentration is increased, titanium to titanium interactions increasingly affect the spectrum. The spin-allowed ligand field bands increase in intensity, and the temperature dependence of the oscillator strength of the $^3T_{1g} \rightarrow {}^3T_{2g}$ transition becomes nonvibronic. A hot band due to an exciton created by a titanium pair or cluster is observed in more heavily doped systems, and at the highest concentration and lowest temperature, broad charge-transfer bands dominate in the visible region. Both orbital and spin selection rules are affected by the titanium to titanium interactions, which appear to be larger than those observed with other first-row transition-metal ions. As a consequence, it is possible to study experimentally the transition from a spectrum due to isolated titanium ions to one that is due to "charge transfer" in the lattice.

Introduction

The optical properties of divalent transition-metal ions in halide layer lattices of the cadmium iodide or cadmium chloride type have been studied in some detail, particularly for compounds of iron,[1,2] cobalt,[3] and nickel[3,4] and for doped systems such as Co^{2+} in $CdCl_2$[5,6] and in $CdBr_2$.[6] The pure materials are metamagnets with both ferromagnetic and antiferromagnetic interactions. The main spin-allowed ligand field transitions are readily identifiable, and much of the detailed work has centered on the characterization of the magnetic domain structure and on an investigation of the magnon-assisted side bands observed in the sharp fine structure of the spin-forbidden transitions in the visible region of the spectrum.

Recently, we have used in situ methods to generate titanium(II) ions in chloride melts[7-9] and have found it possible to grow from the melt single crystals of magnesium chloride containing a wide range of concentrations of titanium(II) ions.[7] The titanium(II) appears to be present in solid solution in the magnesium chloride layer lattice, and in that sense, this system is analogous to the cobalt(II)/cadmium chloride system. However, a greater degree of delocalization of the d electrons would be expected for titanium(II), and it has been found, for example in studies of the magnetic behavior of powders of the divalent chlorides of the first-row transition metals.[10] Further, titanium(II) oxide is a black semiconducting material, and titanium(II) chloride is a brown or black material, which has a spectrum with a broad charge-transfer band in the visible region. Thus, the titanium(II)/magnesium chloride system is ideal for the study of interactions that occur with more delocalized electrons than those involved in the d → d spectra of later transition metals.

In an early experiment a crystal of titanium(II)-doped magnesium chloride was grown by vapor transport. It had a titanium-to-magnesium atomic ratio of 1/5 and could be reversibly switched between the spectrum of a d^2 ion and a charge-transfer spectrum by changing the temperature.[8] In this paper, we report a study of the optical spectrum of titanium(II)-doped magnesium chloride crystals at concentrations up to a 1/5 titanium-to-magnesium atomic ratio.

Materials and Methods

Reagent-grade magnesium chloride was placed in a silica crucible and melted at 800 °C in a muffle furnace overnight. A top layer of magnesium oxychloride and a bottom layer containing black impurities formed. The crucible was allowed to cool in a drybox, and the middle layer of polycrystalline magnesium chloride was recovered. A sample of this middle layer was placed in a silica ampule and the ampule sealed under vacuum. It was suspended in a furnace and melted at 800 °C. A single crystal of magnesium chloride was grown from the melt by the Bridgeman process. The product consisted of clear, well-formed single crystals with a definite cleavage plane. The ampule was broken open in the drybox and the top and bottom of the crystal was discarded. Part of the middle section of the crystal was crushed, and a weighed amount of it was added along with a weighed amount of anhydrous cadmium chloride and pure titanium metal to a second ampule. This was sealed and melted. In the melt, the cadmium chloride reacted with the titanium as

$$CdCl_2 + Ti \rightarrow Cd\uparrow + TiCl_2$$

The cadmium metal sublimed out of the melt and condensed on the neck of the ampule.[9]

Single crystals were grown from the melt as before. When the tubes were cracked open, the middle part of each boule was found to be a single crystal, homogeneously colored either blue or green depending on titanium ion content. Samples with parallel faces were readily cleaved with a razor blade. The z axis of the crystal is expected to be perpendicular to these faces. This was confirmed by an X-ray precession photograph of one sample and examination of all samples by using a polarizing microscope. Part of each crystal was analyzed for titanium and magnesium by atomic absorption spectrometry. Throughout this paper, the titanium-to-magnesium content is expressed as an atomic or ionic weight ratio.

Axial spectra were recorded using a Beckman 1VM spectrophotometer. The samples were mounted on the cold finger of a Displex closed cycle refrigerator with Crycon conducting grease. The thermocouple was placed close to the sample on the cold finger. Previous experiments have indicated that this position produces a lag compared to the sample temperature of less than 1° at 10 K.

Results and Discussion

Magnesium chloride crystals consist of layers of cubic-closed-packed chloride ions with magnesium ions occupying every second layer of octahedral holes in the chloride lattice.[11] The interlayer spacing is slightly less than the ideal distance, producing a trigonally distorted octahedral magnesium ion environment. Lauē X-ray photographs and microscopic examination confirm that the titanium(II)-doped crystals are also layer lattices with an easy cleavage plane perpendicular to the major axis. They are transparent and evenly colored throughout with no evidence of intercolates or other macroscopic inhomogeneities. The spectrum at room temperature contains two bands assignable as the $^3T_{1g}$

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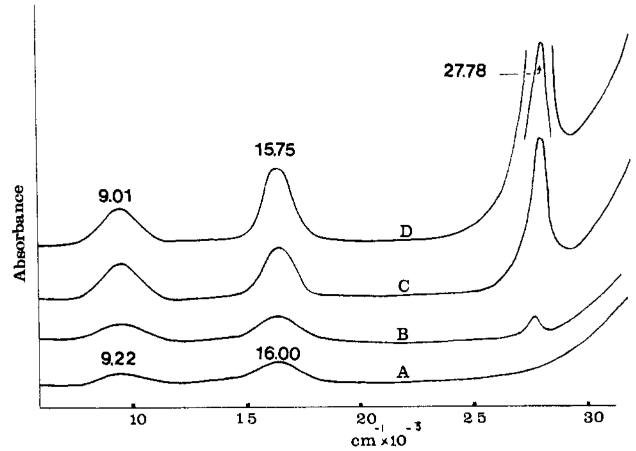

Figure 1. Room-temperature spectrum of titanium(II)-doped magnesium chloride with approximate titanium-to-magnesium atomic ratios of 1/100 (A), 1/50 (B), 1/33 (C), and 1/5 (D). To take account of different crystal thicknesses, absorbance values have been adjusted to represent the same path length for each crystal. The ${}^3T_{1g} \rightarrow {}^3T_{2g}$ transition is at approximately 9000 cm^{-1}, and the ${}^3T_{1g} \rightarrow {}^3T_{1g}$ (${}^3P$) transition is at approximately 15 750 cm^{-1}.

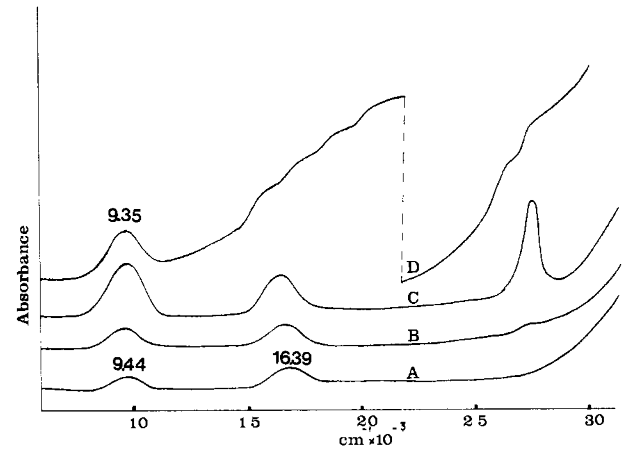

Figure 2. 10 K spectrum of titanium(II)-doped magnesium chloride with approximate titanium-to-magnesium atomic ratios of 1/100 (A), 1/50 (B), 1/33 (C), and 1/5 (D). To take account of different crystal thicknesses, absorbance values have been adjusted to represent the same path length for each crystal.

$\rightarrow {}^3T_{2g}$ (${}^3F$) and ${}^3T_{1g} \rightarrow {}^3T_{1g}$ (${}^3P$) transitions of an octahedrally coordinated titanium(II) ion (d^2) (Figure 1). In the most dilute system, *Dq* and *B* values of 920 and 505 cm^{-1} and the oscillator strengths of the transitions are consistent with octahedrally coordinated titanium(II)[9] (Figures 2 and 3). Thus, the titanium ion lies either on a magnesium site or in one of the octahedral holes in intermediate layers. At higher titanium ion concentrations, titanium ions will occupy adjacent lattice sites to form pairs and clusters of titanium ions separated in the lattice by chlorides. Two chloride ions in contact with each other lie among the line of centers of the titanium ions, and therefore, interactions between neighboring titanium ions are more likely to occur by indirect bonding involving bridging chlorides rather than by a direct interaction between the metal ions. Spectra were recorded from samples with titanium ion concentrations such that the titanium ion sites were predominantly single centers (sample A in Figures 1 and 2), a mixture of single centers and pairs (sample B), and clusters of various sizes (samples C and D).

The temperature dependence of the oscillator strengths of the ${}^3T_{1g} \rightarrow {}^3T_{2g}$ and ${}^3T_{1g} \rightarrow {}^3T_{1g}$ (${}^3P$) single-center transitions observed with sample A can be fitted by using the expression $f = f_0 \coth (h\nu/kT)$, using frequencies for the allowing vibrations of 80 and 119 cm^{-1}, respectively. This behaviur is similar to that of the same transitions in Ti^{2+} in NaCl[9] and other transition-metal ions in centrosymmetric environments[13] (Figure 3). Thus, irrespective

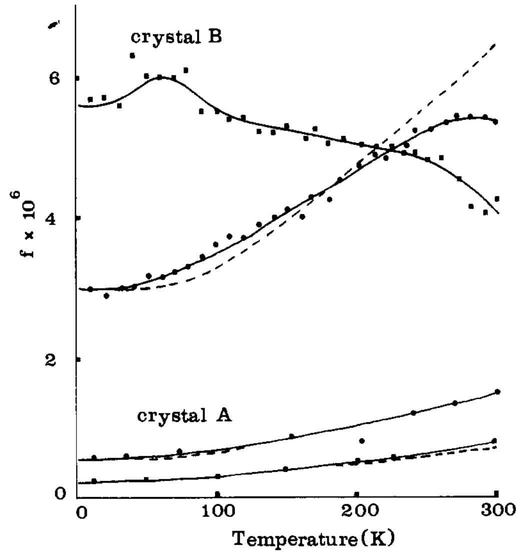

Figure 3. Temperature dependence of the oscillator strengths of the ${}^3T_{1g} \rightarrow {}^3T_{2g}$ (■) and ${}^3T_{1g} \rightarrow {}^3T_{1g}$ (${}^3P$) (●) transitions for the 1/100 (A) and 1/33 (B) crystals. Dotted lines are fits to the coth expression.[11]

of the theoretical validity of the expression, it would seem that by comparison with other systems, the spectra from samples with lower doping levels are characteristic of vibronically allowed d–d transitions in a centrosymmetric environment. The noncentrosymmetric field component from the trigonal field of MgCl$_2$ or from the vacancy associated with the divalent ion in NaCl is not large enough to contribute sufficient intensity to mask the vibronic effect. However, one difference between this crystal and sodium chloride is that the rate of increase in intensity of the ${}^3T_{1g} \rightarrow {}^3T_{2g}$ band is greater, whereas for the ${}^3T_{1g} \rightarrow {}^3T_{1g}$ (${}^3P$) transition the difference between the two systems is small. The fine structure found in the Ti^{2+}–NaCl case demonstrated that there was a different vibronic mechanism for each transition and that the progression observed for the ${}^3T_{1g} \rightarrow {}^3T_{2g}$ transition was a vibration of the impurity site rather than the host lattice. It is now clear that the allowing vibration is also a vibration of the site and is sensitive to changes in environment.

At higher titanium ion concentrations, the maxima of the ligand field bands at room temperature and at 10 K shift to lower energies due to the increasing influence of the larger, softer titanium ions on the host lattice. In addition, the oscillator strengths of the two transitions behave in different ways. For example, in the 1/33 sample the oscillator strength at 10 K of both transitions is very much greater than that expected for an isolated ion in a centrosymmetric environment. The ${}^3T_{1g} \rightarrow {}^3T_{2g}$ band is the larger of the two, and compared to the 1/100 values, the intensity is increased about 30-fold at 10 K and there is a decrease in intensity when the temperature is raised. An additional increase in the intensity of this transition at about 80 K is possibly due to the formation of magnetic domains in the system. The oscillator strength of the ${}^3T_{1g} \rightarrow {}^3T_{1g}$ (${}^3P$) transition is greater by a factor of about 6 at 10 K in the 1/33 sample. It increases by a larger amount than for the isolated ion as the temperature is raised, and the fit to the coth expression is poor. Above about 250 K, oscillator strengths of both transitions tend to decrease. This is likely to be due to the effect of increased thermal motion overcoming titanium–titanium interactions.

In the Ti^{2+}–NaCl systems[9], no spin-forbidden transitions were observed except for some weak structure close to the peak of the ${}^3T_{1g} \rightarrow {}^3T_{1g}$ (${}^3P$) band, which could equally well have been due to some ill-defined vibronic effect. This structure can again be observed in the MgCl$_2$ crystals, suggesting that the vibronic argument is unlikely. In addition, there is some weak, ill-defined structure in the region of 24 500 cm^{-1} in the 1/1000 spectrum at 10 K, which in the 1/50 and 1/33 spectra is resolved into a series

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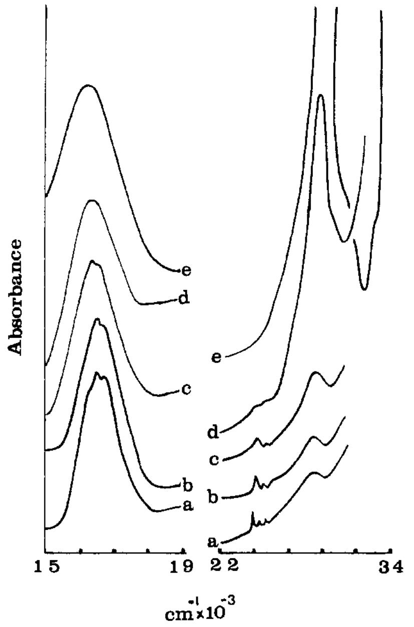

Figure 4. Temperature dependence and fine structure of the visible spectrum of the 1/50 crystal: a, 10 K; b, 20 K; c, 50 K; d, 100 K; e, 295 K.

of peaks of greater intensity relative to the spin-allowed bands (Figure 4). If these bands had the same intensity relative to the spin-allowed d–d bands in the sodium chloride system, they would have been detected relatively easily. Thus, these bands would appear to be dependent on Ti–Ti interactions in the system and may include magnon-assisted side bands analogous to those found for other transition-metal ions.[1-6] Figure 4 also indicates that the peak position of the $^3T_{1g} \rightarrow {}^3T_{1g}$ (^3P) transition in the 1/50 crystal shifts to higher energies between 295 and 100 K. This is as expected for a vibronic system. The charge-transfer band edge also moves toward higher energies as the temperature is lowered.

Two additional features of the spectra that appear to be due directly to titanium interactions are identifiable. These are a discrete band, which in the 1/50 crystal (B) is a hot band but which, as the titanium ion concentration is increased, has a decreased temperature dependence, and a charge-transfer band system, present in the 1/5 crystal at 10 K. Doped halides of the $MgCl_2$ type have been shown to produce excitons as a result of the interaction of the metal ion dopant with the lowest energy bands of the host crystal,[15] and the 27 777-cm^{-1} band is probably due to an exciton arising from a higher energy level of the pair or cluster ground state. The change in temperature dependence as the titanium ion concentration increases reflects the effect of cluster formation. The charge-transfer system arises as a result of more extensive titanium–titanium ion interactions in the lattice. Dilution of those interactions by the addition of magnesium leads to a situation where thermal motion can disrupt the long-range order creating localized clusters. Thus, in the 1/5 sample, the low-temperature spectrum resembles that of titanium dichloride, whereas the room-temperature spectrum resembles that from the 1/33 crystal at room temperature and 10 K.

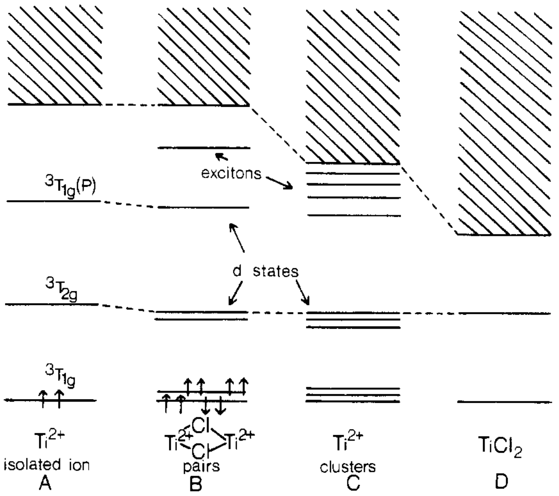

Figure 5. Simplified diagram of the system which gives rise to the observed spectra: (A) dilute solution of titanium(II) in magnesium chloride; (B) titanium pairs, (C) large titanium clusters, (D) titanium dichloride. This diagram ignores spin-forbidden transitions and splittings due to the trigonal field and spin–orbit coupling.

Figure 5 illustrates four idealized situations that will arise, namely an isolated titanium ion in a magnesium chloride host lattice, a pair of titanium ions interacting through the intervening chlorides, larger localized titanium chloride clusters, and a band of titanium and chloride ions such as would be present in titanium dichloride. Since the ligand field bands studied are due to spin-allowed transitions, the orbital selection rules are likely to have a considerable influence on the intensity. The most likely source of the additional intensity is by a mixing of the p orbitals from the intervening chloride ions with the d orbitals of the titanium ions. Such static mixing would be possible in the pair state and would not be expected to occur for transitions arising from single centers with essentially octahedral symmetry.

Any explanation of these results is necessarily qualitative since they represent a first experimental investigation of a system where the greater degree of delocalization of the d orbitals causes a more substantial interaction between the metal ions than that usually found later in the transition-metal series. However, the spectra indicate changes in bonding characteristics, which place the detailed theoretical analysis in the area between single-center theories such as ligand field theory and band theory. This is an area which itself represents a significant theoretical challenge at the present time, but the system does illustrate types of behavior which require a more detailed theoretical explanation.

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Registry No. Ti^{2+}, 15969-58-1; $MgCl_2$, 7786-30-3.

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