ENERGY TRANSFER IN ONE-, TWO-, AND THREE-DIMENSIONALLY COUPLED SALTS OF DIVALENT MANGANESE

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Received 29 August 1979

The emission spectra of several antiferromagnetic complexes of divalent manganese ($CsMnBr_3$, Rb_2MnCl_4, $CsMnCl_3$ and $KMnCl_3$) which contain rare-earth ion impurities have been studied as a function of temperature. In all cases there appears to be a thermally activated energy migration which often results in an efficient transfer of electronic excitation from the manganese to the rare-earth impurities.

1. Introduction

A rapid thermally assisted migration of electronic excitation energy has been observed in crystals of the antiferromagnetic manganese salts, $(CH_3)_4NMnCl_3$ (TMMC) and $CsMnBr_3$. McClure and co-workers determined that the manganese excitation in TMMC begins to migrate above 50 K [1]. At room temperature the migration is extremely rapid with the hopping time for excitons being on the order of 10^{-12} s. They also found that the excitation energy is trapped by ions such as Co^{2+}, Ni^{2+}, and Cu^{2+} when these ions are doped into crystals of TMMC. Above 50 K, the intensity of the manganese emission from the doped crystals decreases with increasing temperature as a result of the energy transfer from the manganese to the impurities. No impurity emissions were detected which suggests that the foreign ions behave primarily as non-radiative traps. In $CsMnBr_3$, where the energy migration appears to be qualitatively similar to that of TMMC, emission from impurities has been observed [2]. Crystals of $CsMnBr_3$ doped with neodymium show an emission characteristic of Nd^{3+} which is stimulated by energy transfer from the manganese. At room temperature the neodymium emission is quite intense, at least an order of magnitude stronger than the emission from manganese. As the doped crystals are cooled the rate of energy transfer decreases so that the manganese emission gains intensity at the expense of the emission from Nd^{3+}.

The observation of an impurity emission is particularly important since it is then possible to directly monitor the migration and transfer of electronic excitation energy in the doped crystal. This communication describes investigations which explore the generality of the manganese to rare earth energy transfer process. The emission spectra of several antiferromagnetic manganese salts doped with a variety of rare earth ions have been studied. These salts, $CsMnBr_3$, Rb_2MnCl_4, $CsMnCl_3$ and $KMnCl_3$, represent materials in which the predominant magnetic interactions occur in one, two or three dimensions. Energy transfer was observed in all of the salts with Nd^{3+}, Ho^{3+}, Er^{3+}, and Tm^{3+} behaving as radiative traps for the manganese excitation. In these materials the lowest excited state of the divalent manganese, the $^4T_1$, lies above the $^6A_1$ ground state by approximately 16000 to 18000 cm^{-1}. As shown in fig. 1 the rare earth impurities produce a number of emissions in the 9000 to 16000 cm^{-1} region which arise through a rapid energy transfer in the doped crystals. Crystals doped with Pr^{3+} and Eu^{3+} were also studied;

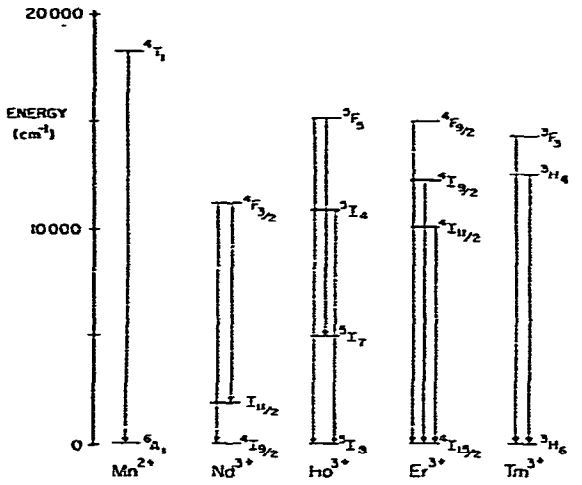

Fig. 1. Energy level diagram showing the rare earth transitions which have been identified in the emission spectra of the doped manganese salts.

however, no rare earth emissions were detected between 9000 and 16000 cm^{-1}.

Although there are noticeable differences between the salts, the migration and transfer of the manganese excitation energy conforms to the general pattern observed in TMMC and $CsMnBr_3$. It appears that in all of the salts, energy transfer requires some type of thermal activation. At high temperatures (above 200 K) the energy transfer between the divalent manganese and the rare earth impurities is quite rapid and often very efficient. Fig. 2 shows the emission and excitation spectra of a Rb_2MnCl_4 crystal doped with Tm^{3+} and recorded at room temperature. The behavior of this crystal is typical of most of the doped crystals above 200 K. The emission spectrum is characteristic of the rare earth while the excitation spectrum shows a close correspondence to the absorption spectrum of the pure manganese salt. As the doped crystals are cooled the rate of energy transfer decreases and the intensity of the rare earth emission begins to diminish. Eventually the rare earth emissions become very weak as the manganese excitation is effectively localized. During this process the intensity of the manganese emission increases dramatically. The following sections contain brief descriptions of each of the manganese salts used in this study.

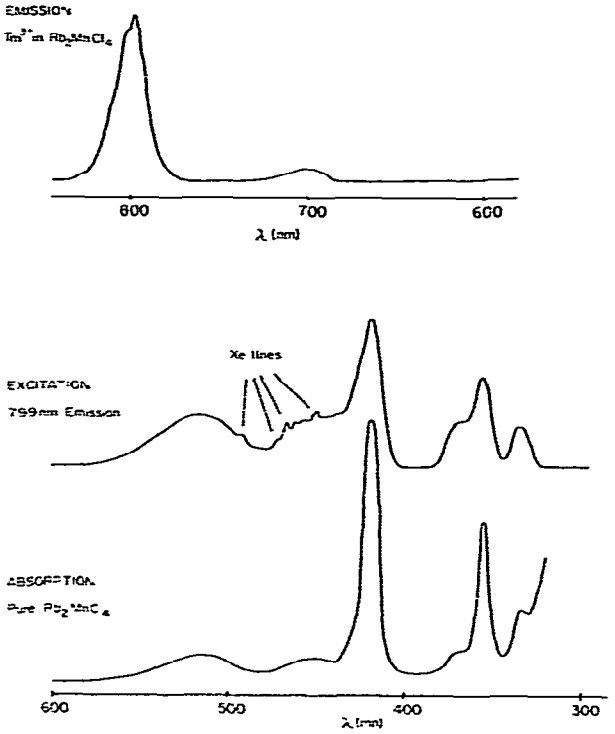

Fig. 2. Emission and excitation spectra of a Rb_2MnCl_4 crystal doped with Tm^{3+} recorded at room temperature. The intense emission at 799 nm corresponds to the $^3H_4 \rightarrow {}^3H_6$ transition of Tm^{3+} while the weaker feature at 700 nm results from the $^3F_3 \rightarrow {}^3H_6$ transition. The excitation spectrum was obtained by monitoring the Tm^{3+} emission at 799 nm. The room temperature absorption spectrum of pure Rb_2MnCl_4 is included for comparison.

2. $CsMnBr_3$

Diffraction studies show that $CsMnBr_3$ adopts a hexagonal structure isomorphous with $CsNiCl_3$ [3]. In this structure, the $[MnBr_6]^{4-}$ octahedra share opposite faces to form infinite linear chains which have the stoichiometry, $[MnBr_3^-]_n$. Magnetic susceptibility and neutron scattering studies indicate that $CsMnBr_3$ is a quasi-one-dimensional antiferromagnet [4,5]. The intrachain interaction is about 7 cm^{-1} which is roughly 500 times greater than the interchain coupling. It appears that unless small monovalent ions such as Li^+ are present trivalent ions tend to cluster in pairs when introduced

as impurities into crystals which adopt the $CsNiCl_3$ structure [6–8]. Crystals of $CsMnBr_3$ doped with Nd^{3+} and Li^+ were studied along with crystals containing only Nd^{3+}. The energy transfer seems to be similar in both cases. Crystals containing Er^{3+} and Tm^{3+} show intense rare earth emissions (which indicates that these ions are effective traps for the manganese excitation. In contrast, samples doped with Ho^{3+} show no rare earth emission. The reason for this is not clear, since Ho^{3+} emissions are observed in the other manganese salts. The behavior of the emission spectrum as a function of temperature depends to some extent on which rare earth is present in the doped crystal. In general, however, it appears that the rate of energy transfer begins to diminish below 100 K. At 30 K there is little evidence of energy transfer in any of the samples.

3. Rb_2MnCl_4

The salt, Rb_2MnCl_4, crystallizes in a layered structure isomorphous with K_2NiF_4 [9]. The material is reported to behave as a two-dimensional antiferromagnet with an inplane interaction of approximately 4 cm^{-1} [10,11]. The magnetic susceptibility passes through a maximum around 100 K. Crystals doped with Nd^{3+}, Ho^{3+}, Er^{3+}, and Tm^{3+} produce intense rare earth emissions which indicates an effective energy transfer. There is not much evidence of a decrease in energy transfer until the doped crystals are cooled below 70 K. In some samples there is significant transfer even when the temperature is less than 30 K. The intensity of the manganese emission increases by more than an order of magnitude between 70 K and 30 K. The temperature dependence of the manganese emission from the doped crystals is quite similar to that reported for pure Rb_2MnCl_4 [12].

4. $CsMnCl_3$ and $KMnCl_3$

There have been several structural investigations of $CsMnCl_3$ [13–15]. The material adopts a hexagonal lattice which contains linear $[Mn_3Cl_{12}]^{6-}$ units composed of three $[MnCl_6]^{4-}$ octahedra sharing faces. These trimeric units share corners to form a three-dimensional array. The lattice constants of $KMnCl_3$ suggest that the salt is a tetragonal perovskite at room temperature [16]. Above 731 K $KMnCl_3$ is cubic. The perovskite structure can be described as a three-dimensional array of $[MnCl_6]^{4-}$ octahedra sharing corners. In both materials the magnetic interactions would be expected to be three dimensional. It appears that a three-dimensional antiferromagnetic ordering occurs in both salts [13,17,18]. The Néel temperatures for $CsMnCl_3$ and $KMnCl_3$ are 69 K and 100 K, respectively. Rare earth emissions are observed in crystals of both salts doped with Nd^{3+}, Ho^{3+}, Er^{3+}, and Tm^{3+}, although the emission from Ho^{3+} in $CsMnCl_3$ is relatively weak. In $CsMnCl_3$ the energy transfer begins to decrease noticeably below 180 K. At 80 K the rare earth emissions are very weak. The energy transfer in $KMnCl_3$ persists to around 120 K. It diminishes steadily until the transfer is quite weak at 50 K. In neither salt is there a dramatic change when the temperature passes through the Néel point. Like Rb_2MnCl_4, the temperature dependence of the manganese emission from the doped crystals closely resembles that reported for pure $CsMnCl_3$ and $KMnCl_3$ [19]. In $CsMnCl_3$ the manganese emission increases dramatically from 200 K to 100 K. Below 100 K the intensity is essentially constant. The intensity of the manganese emission from $KMnCl_3$ grows noticeably between 100 K and 50 K and remains relatively unchanged below 50 K.

5. Conclusions

A thermally activated energy migration appears to be a common characteristic of magnetically coupled manganese salts. A variety of rare earth ions can serve as radiative traps for the manganese excitation. Among the salts used in this study, the extensive energy transfer persists to the lowest temperatures in Rb_2MnCl_4 and is quenched at the highest temperatures in $CsMnCl_3$. The energy migration and transfer process does not appear to have a dramatic dependence on the dimensionality of the magnetic interactions in the solid.

Acknowledgement

This work was supported by National Science Foundation Grant CHE-77-12557.

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