CLASSIFICATION OF OPTICAL ABSORPTION SPECTRA IN 2D ANTIFERROMAGNET [NH$_3$(CH$_2$)$_n$NH$_3$]MnCl$_4$ ($n=2,\ldots,5$)

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ABSTRACT

Optical absorption spectra in [NH$_3$(CH$_2$)$_n$NH$_3$]MnCl$_4$ ($n=2,\ldots,5$) were investigated. In the transitions of $^6A_{1g}(S)\rightarrow ^4A_{1g}(G)$, $^4E(G)$, $^4T_{2g}(D)$ and $^4E_g(D)$, a lot of fine structures caused by electric dipole transition appeared at 4.2K. It was concluded by taking into account the temperature dependence that these fine structures resulted from magnon assisted transitions.

In these compounds, when the magnetic field is applied along the spin easy axis, a drastic spectral change occurs at about 30K Oe, which is due to the spin flop transition. The spectral shifts at the spin flop transition can be numerically reproduced, and the fine structures of the absorption spectra $^6A_{1g}(S)\rightarrow ^4A_{1g}(G)$, $^4E(G)$ and $^4T_{2g}(D)$ can be assigned. It is concluded that the spectral shift at the spin flop transition is one of the most powerful methods to assign the absorption spectra in magnetic compounds.

1. INTRODUCTION

Among magnetic insulators, a large number of low dimensional systems have attracted much interest and have been studied extensively during the past fifteen years. Among such materials, perovskite type complex [NH$_3$(CH$_2$)$_n$NH$_3$]MX$_4$ ($M=Mn, Cu$, $X=Cl, Br$, $n=2,\ldots,5$) of the so called alkylene ammonium family and (C$_n$H$_{2n+1}$NH$_3$)$_2$MX$_4$ (alkyl ammonium family) are famous, both for their magnetic properties[1,2], and for their successive structural phase transitions.[3] In these crystals, nearly quadratic layers consist of magnetic metal ions, and these ions are surrounded octahedrally by six halogen ions, four of which share corners of the octahedra (Fig. 1). These two dimensional networks are widely separated by non magnetic alkylene or alkyl ammonium groups, so that these materials show the quasi two dimensional magnetic behaviour.

In the case of $M=Mn$ alkylene ammonium family, spins are ordered antiferromagnetically parallel to its easy axis (b-axis: perpendicular to the layer) below Neel temperature $T_N$ (~40K). This family can be considered as an ideal $S=5/2$ two dimensional Heisenberg antiferromagnetic system as well as $M=\text{Mn}$ an alkyl ammonium family ($j'/j=10^{-4}-10^{-18}$, j and j' are intra and inter layer exchange interactions, respectively)[4].

It is well known that Mn spins flop into the 2D layer when an external magnetic field $H_0$ (parallel to the easy axis) exceeds the critical field $H_{SF}$. This magnetic phase transition is known as spin-flop (SF) transition. The optical absorption spectra of the title complexes make drastic shifts at the SF-transition. The purpose of the present paper is to investigate the cause of this spectral change and to classify the optical absorption spectra into their original excitons by taking into account this spectral change at the spin-flop transition.
2. EXPERIMENTAL PROCEDURE

To prepare the compounds, nearly equivalent stoichiometric amounts of manganese chloride (MnCl₂·4H₂O) and alkylene diammonium chlorides were dissolved in water which was slightly acidified with hydrochloric acid, and then single crystals were precipitated by slow evaporation.

For the spectroscopic measurements, a helium cryostat and a grating spectrometer were used. The photoelectric signal detected by a photomultiplier and amplified by a lock-in amplifier was converted into logarithmic scale and then recorded on a chart paper. The magnetic field dependence of the spectra was obtained with a Helmholtz-type superconducting magnet, which produces the maximum field of 60kOe.

3. SPECTRA AT ROOM TEMPERATURE

Figure 2 shows the optical absorption spectra of the compound (n=3) at room temperature (17000-30000cm⁻¹). Crystalline field parameter and Racah parameters were determined by fitting the experimental and calculated energy values of ⁴A₁g(G), ⁴T₂g(D,G) and ⁴E (D,G) states taking into account the configuration interaction. Results were as follows; Dq=550cm⁻¹, B=750⁻¹ and C=3100cm⁻¹.

In this region, there appeared a lot of fine absorption lines which are electric dipole transitions at low temperature. From the measurements of the temperature dependence of the energy position and the integrated intensity of the lines, they were considered to be magnon assisted transitions and to be classified into four groups A, B, C and D as shown in Fig. 3, taking into account total spectral aspects of fine structures. Each group consists of several lines which are labelled as A-1,A-2,...,D-3.

Fig. 3 shows the magnetic field dependence of the spectra corresponding to the ⁶A₁g(S)→⁴T₂g(D) and ⁴E (D) transitions in (NH₃(CH₂)₃NH₂)MnCl₄.
The spectra in this region of this alkylene diammonium family (n=2,···,5) are similar to each other especially with regard to their line shapes. These spectra show similar behavior when external magnetic fields \( H_0 \) are applied.

In the case of the propylene diammonium compound (n=3), a remarkably sharp SF-transition was reported at \( H_0=24.55 \text{kOe} \) in magnetic susceptibility measurements, where the optical absorption spectra make drastic shifts as shown in Fig.4(a). The magnitude of the spectral shifts at the SF-transition is listed in Table 1. As shown in Table 1, the peaks A-1, A-3 and A-4 shift to the lower energy side at \( H_0=H_{\text{SF}} \), while the peak A-2 shifts to the higher energy side. The peaks B-1,2,3,4 shift to the higher energy side, while the peaks C-1,2,3 shift to the lower energy side. The peaks D-1,2,3 which appear at the highest energy region shift to the higher energy side.

In order to explain these spectral shifts, the following Hamiltonians are employed for the ground state \((\tilde{A}_{1g})\) and the excited states \((\tilde{T}_{2g}, \tilde{E}_g)\).\(^5\)

\[
H^{\text{eff}}(\tilde{A}_{1g}(S)) = 2\mu_B H^*_{\text{ex}} + D S_z^2 + 2\mu_B H_0^* 
\]

and

\[
H^{\text{eff}}(\tilde{T}_{2g}(D), \tilde{E}_g(D)) = 2\mu_B H^*_{\text{ex}} + \mu_B \tilde{H}_0 (2S+L) + V(E\tilde{g}) + V(T_2 \tilde{g}) + H_{\text{SO}}^* 
\]

where \( H^*_{\text{ex}} \) is the internal magnetic field for the excited state, \( V(E\tilde{g}) \) is the tetragonal field, \( V(T_2 \tilde{g}) \) is the rhombic field, and \( H_{\text{SO}}^* \) is the spin-orbit interaction. Exciton energy levels are given by comparing the experimental results with calculated ones which are obtained by diagonalizing the above Hamiltonians in both the antiferromagnetic and the spin-flop phases. According to our calculation, the spin-orbit coupling constant \( \zeta \) which appears in the off diagonal matrix elements, determines the energy shifts due to the SF-transition, and the low symmetry fields determine the splitting of the electronic energy levels. As shown in Fig.4, by setting \( \zeta=250 \text{cm}^{-1}, \tilde{C}_{\text{2g}}(D)||V(E\tilde{g})||\tilde{T}_{2g}(D)=-825 \text{cm}^{-1}, \tilde{C}_{\text{2g}}(2g)||V(T_2 \tilde{g})||\tilde{T}_{2g}(D)=450 \text{cm}^{-1} \) and \( \tilde{H}=32 \text{cm}^{-1} \), the spectral shifts could be reproduced quantitatively. Among these levels, a-1, a-2,···,b-4 excitons mainly consist of \( \tilde{T}_{2g}(D) \) state and c-1, c-2,···,d-4 excitons mainly consist of \( \tilde{E}_g(D) \) state.

Now the ground multiplet is sextet, and the measuring temperature (1.5K) was sufficiently below \( T_N \) so that \( M_s \) of the ground state is considered to be \( M_s=-5/2 \). On the other hand, the transition is doubly forbidden (parity and spin), so that the change of \( M_s \) due to the
The transition can be considered as at most $\Delta M_s = 1$. Therefore the spin component of the observable excited state $^4T_{2g} (D)$ must be $M_s = -3/2$. The numbers written in Fig. 4(b) show the percentage of the $M_s = -3/2$ components in the total wave functions. Consequently, the peak A-1 is considered as the magnon sideband of the a-1 exciton, and A-2 as the magnon sidebands of the a-2 exciton. In the similar way, other peaks can be classified into their original electronic excitations. These results are listed in Table 1.

As mentioned above, the optical absorption spectra are assigned in the $^4T_{2g} (D)$ and the $^4E_g (D)$ region of compound n=3, and similar consideration is available for the other spectral regions and also for other compounds.

5. CONCLUSIONS

The obtained results are summarized below.

1. Analysis of the spectral change due to the spin flop transition is one of the most powerful methods of classifying the absorption spectra in magnetic compounds.

2. The spin-orbit interaction parameter $\zeta$ and low symmetry fields can be determined in this analysis.

3. Spin-orbit interaction plays an important role in the spectral shifts at the spin-flop transition.

<table>
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<th>Peak</th>
<th>energy (cm$^{-1}$)</th>
<th>$\Delta E$ (cm$^{-1}$)</th>
<th>original exciton</th>
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<td>A-1</td>
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</table>

(a) Energy difference of peaks between AF-phase and SF-phase, $\Delta E = E($SF-phase$) - E($AF-phase$)$

(*) The peak B-2 is not listed in this table since its position is not clear in SF-phase.

REFERENCES

1) R.D. Willet and E.P. Riedel; Chem. Phys., 8(1975)112
3) R. Kind, S. Plesko and J. Rocs; Phys. stat. sol. (a) 47(1978)233
4) L.J. De Jongh and A.R. Miedema; Adv. in Phys., 23(1974)1