FIELD INDUCED DAVYDOV SPLITTING IN QUASI-ONE-DIMENSIONAL ANTIFERROMAGNETS CsMnCl₃·2H₂O AND (CH₃)₂NH₂MnCl₃·2H₂O

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ABSTRACT

Optical absorption spectra corresponding to the ⁶A₁g→⁴T₂g (D) transition in CsMnCl₃·2H₂O and (CH₃)₂NH₂MnCl₃·2H₂O were investigated under magnetic fields. In these compounds, a sharp exciton line in the lowest energy region of this transition was split by the applied field perpendicular to the spin direction. From the analysis of the spin configuration, it was proved to be a Davydov splitting induced by the field. The field induced Davydov splitting can be explained by the fact that in an external magnetic field perpendicular to the spin direction, spins cant towards the field so as to remove the prohibition of the inter-sublattice exciton transfer. The field dependence of this splitting was explained by the exciton transfer due to the anisotropic exchange interaction.

1. INTRODUCTION

It is known that the exciton transfer, which is the origin of the Davydov splitting, in magnetic insulators depends on the spin configuration of the crystals.[1] In RbMnF₃[2], for example, it was found that the exciton lines corresponding to the ⁶A₁g→⁴E₄(G) transition are split due to the exciton transfer among sublattices, of which spins are canted by an external magnetic field. The magnitude of the splitting is proportional to \(\sin^2(\theta/2)\), where \(\theta\) is the angle between two spins on the sites between which the exciton transfer occurs. Later, this magnetic field dependence was explained[3] by the introduction of the generalized exchange Hamiltonian referring to the individual d-orbitals which constitute the ground state ⁴E₄(G) of Mn²⁺.

We have investigated the absorption spectra of CsMnCl₃·2H₂O (CMC) and (CH₃)₂NH₂MnCl₃·2H₂O (DMMC·2aq) and observed Davydov splittings induced by external magnetic fields. Both compounds consist of chains made up by Cs[S-Mn(H₂O)₂Cl₄]₂⁻ octahedra, hence they are quasi-one-dimensional antiferromagnets. The exchange interaction [4], the Neel temperature, and the field \(H_c\) where spin-flop transition occurs are 3.0K, 4.89K and 17.9kOe(at 1.8K), respectively for CMC [4] and 2.7K, 6.36K and 13.9kOe(at 1.8K), respectively for DMMC·2aq [5]. In CMC, the spins are directed along the b-axis(easy axis) [6] in the antiferromagnetic phase and along almost the c-axis(intermediate axis) [7] in the spin-flop phase, and then the hard axis is the a-axis. For DMMC·2aq, the easy, intermediate and hard axes are the a-, b- and c- axes, respectively, however the directions of the spins in ordered phases have not yet been determined. For both compounds, quite contrary to the case of RbMnF₃, the magnitude of the splitting seems not to be proportional to \(\sin^2(\theta/2)\). By the use of the effective Hamiltonian which operates only on the total spins of the ground and excited states, it was found that the exciton transfer is reduced by the discrepancy between the canting angles of the spins for the ground and excited state.

2. EXPERIMENTAL PROCEDURE

Single crystals of CMC and DMMC·2aq were prepared by slow evaporation of the aqueous solution containing equimolar quantities of MnCl₂·4H₂O and CsCl or (CH₃)₂NHCl, respectively.
For optical absorption measurement, the samples were immersed in liquid helium of which temperature was lowered down to 1.8K by pumping. Magnetic field up to 61kOe was produced by a Helmholtz type superconducting magnet. A Jobin-Yvon THR-1500 spectrometer was used with an iodine lamp as a source of light. And the light signal was converted to electric signal, which was recorded by a chart recorder. Photographic method was also used with a spectrometer equipped with a holographic grating with 1200 line/mm and of 110mm wide. In this case, magnetic field was provided by a 28kOe electromagnet and the light source was a xenon lamp. The angular dependence of the spectra on the direction of the magnetic field was also measured photographically by rotating the sample around the axis parallel to the light pass.

3. EXPERIMENTAL RESULTS

As is well known, in the lowest energy side of the absorption band corresponding to the $\tilde{6}A_{1g}^{4}T_{2g}^{4}$ transition in CMC, a sharp line appears at 26736.7cm$^{-1}$ (hereafter called C-line). The C-line can be observed in the spectra with polarization vector $\tilde{b}$/b and $\tilde{c}$/c. When an external magnetic field was applied to the b-axis and $|H_{0}|<H_{C}$(H$\perp$/b(AF) case), the C-line became broader with increasing strength of the magnetic field (Fig.3). When the crystal was in the spin-flop phase ($H_{0} \parallel c$) (H$\perp$/b(SF) case), two absorption lines appeared. The C-line was split into two lines when the field was parallel to the a-axis (H$\perp$/a case) or the c-axis (H$\perp$/c case), and the splitting became larger with increasing strength of the field for the both cases.

In order to determine whether the two lines in the H$\perp$/b(SF) case correspond to the split lines in the H$\perp$/c case, a field of 28kOe was applied perpendicular to the a-axis and the behavior of the spectrum was traced in the rotational field. The result is plotted in Fig.4, which shows that the two lines in the H$\perp$/b (SF) case also originate from the C-line.

Now, let us consider the nature of the splittings of the C-line. In the ordered spin phase, Kramers doublets of a Mn$^{2+}$ ion are split by the exchange interaction, hence all states of Mn$^{2+}$ ion are nondegenerate. When an external field is applied to a certain direction, only the symmetry elements which keep the direction of the external field unchanged are allowed as the symmetry elements of the system. On the basis of the chemical and the magnetic structure of CMC, it can be shown that all eight sites of Mn$^{2+}$ in the magnetic unit cell are equivalent in the cases of H$\perp$/a, /c and //b(SF). Therefore, it is concluded that the splitting of the C-line observed in the H$\perp$/a, /c and //b(SF) cases is the Davydov splitting.

Investigation of the absorption bands in DMMC·2aq revealed that a sharp exciton line appears at 26823.3cm$^{-1}$ (hereafter called D-line), in the lowest energy region of the $\tilde{6}A_{1g}^{4}T_{2g}^{4}$.
The behavior of the D-line was examined in the magnetic fields along three principal axes of the rhombic system. (Fig. 5) When an external magnetic field $H_0$ was parallel to the a-axis, the D-line was not split in the antiferromagnetic phase, while in the spin-flop phase, several exciton lines appeared. In the case of $H_0//b$, the D-line was split into two lines, and the splitting became greater with increasing $|H_0|$. In the case of $H_0//c$, the splitting of the exciton line is not so large as in the case of $H_0//b$.

Similar to the case of CMC, by the rotation of the external field of 28kOe around the c-axis and by the observation of the behavior of the split absorption lines, it was found that the two lines (pointed by dotted arrows in Fig. 5(a)) originate from the D-line. (Fig. 6)

The close resemblance of the magnetic behavior of the D-line of DMMC·2aq to that of the C-line of CMC indicates that the D-line also exhibits the Davydov splitting in magnetic fields.

4. DISCUSSION

Since CMC and DMMC·2aq are quasi-one-dimensional antiferromagnets, it is reasonable to consider that the exciton transfer occurs only along the magnetic chain. In this model, the exciton dispersion is described as (1),

$$E_n(k) = E_0 + 2J_{tr} \cos(kd) - \frac{\pi}{2d} \frac{d}{dx} \frac{d}{dx}$$

where $E_n$ is the energy at the zone boundary, $H_{tr}$ the exciton transfer Hamiltonian, $d$ the distance between neighboring ions, $\psi_{1,2}$ (i=1,2, f=g,e) a wave function of an ion which belongs to the sublattice i, and g and e denote the ground and the excited states, respectively. Therefore, the magnitude of the Davydov splitting is equal to $4|J_{tr}|$, since the states near the zone center are excited in the process of the pure electronic transition.

Now let us analyze the exciton transfer in the case that the external field is applied perpendicular to the direction of the spins ordered at low temperature. The exciton transfer occurs when the spin prohibition rule is relaxed by the canting of the spins. Therefore, we defined the Hamiltonian for exciton transfer as follows:

$$H_{tr} = 2K_1 t_2 + D_2 (c_i \cdot c_{i+1}) + (\text{hermitian conjugates})$$

where $K$ is a scalar constant, $D$ a vector constant, and $c_i (i=1,2)$ is the operator defined in Ref. 8. The first and the second terms in $\Psi_{1,2}$ (1) are analogies of an isotropic exchange interaction and an anisotropic one at the ground state, respectively. Furthermore, the wave functions are replaced by pure spin functions;
$\Psi_{i}^{R} = S_{i}^{z} - (i = 1, 2, \text{or } g, e)$,

where $S_{i} = S_{e} = 5/2, S_{g} = 3/2$, $\theta_{g}$ and $\theta_{e}$ are canting angles of the ground and excited state spins from the easy axis, respectively.

If the easy, hard and intermediate axes are named as $Z_{e}$, $X_{e}$ and $Y_{e}$-axes, respectively, and if it is assumed that the spins incline to the direction of the external magnetic field, the values of the $J_{tr}$ are obtained as follows:

$H_{0} / (X) : \cos^{2} \theta_{g} \cos^{2} \theta_{e} \sum_{q=0}^{q} \sin^{2} \theta_{g} \sin^{2} \theta_{e}$ (2),

$H_{0} / (Y) : \cos^{2} \theta_{g} \cos^{2} \theta_{e} \sum_{q=0}^{q} \sin^{2} \theta_{g} \sin^{2} \theta_{e}$ (3),

(\theta_{g} \theta_{e} etc.).

Since single ion anisotropy in CMC and DMMC·2aq is small, the canting angle $\theta_{g}$ can be calculated from the equation

$\sin \theta_{g} = \frac{H_{0}}{2 \sqrt{s_{g}}} 
\sin \theta_{g}$.

Therefore, in the square brackets of Eqs. (2) and (3), the first and the second terms are almost proportional to $|H_{0}|^{2}$ and $|H_{0}|$, respectively, as long as $|H_{0}|$ is not so large. On the other hand, the $\theta_{e}$ contributes only through the factor $\cos^{2}(\theta_{g} - \theta_{e})/2$, which means that the exciton transfer is reduced by the discrepancy between the canting angles of the spins for the ground state and the excited state. The magnitude of the splitting obtained experimentally are shown in Fig.7. For both compounds, the splittings become greater with increasing $|H_{0}|$. However, it is very different from the magnetic field dependence of the Davydov splitting in RbMnF$_{3}$, of which magnitude is almost proportional to $|H_{0}|^{2}$, as was explained from the isotropic exciton transfer. On the contrary, in CMC and DMMC·2aq, it seems that the exciton transfer is not simply isotropic. And the convexity of the curves of splittings in CMC indicates that the difference of the $\theta_{g}$ and $\theta_{e}$ becomes larger with increasing $|H_{0}|$.

REFERENCES