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Magnetic field effects on the optical spectrum of the quasi-one-dimensional ferromagnet $CsFeCl_3$

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Absorption spectra of $CsFeCl_3$ with a one-dimensional ferromagnetic exchange interaction have been studied in applied magnetic fields up to 26 T along the easy plane. The absorption intensity of the E band, which appears around 500 nm, is found to decrease exponentially with increasing field and a slight residual intensity is found at high fields. The exchange-field approximation is used in the analysis for the ferromagnet with a singlet Fe^{2+} ground state separated from the upper doublet by the trigonal crystal field. The field and temperature dependences can be explained well by the model that the E band consists of not only a hot magnon sideband but also a cold magnon sideband. This is the first confirmation of the presence of a cold magnon sideband in a ferromagnet.

I. INTRODUCTION

Of the various quasi-one-dimensional (1D) ABX_3-type (where A is an alkali-metal ion, B a transition-metal ion, and X a halide ion) magnetic insulators, the three crystals $CsNiF_3$, $CsFeCl_3$, and $RbFeCl_3$ are known to have a short-range ferromagnetic spin coupling along the hexagonal c-axis chain which is much stronger than the antiferromagnetic interchain spin coupling. These 1D ferromagnets have recently attracted much attention, particularly with regard to their phase transitions.[1] Interest in the optical properties has been also increasing in recent years.[2-8] A current topic of interest is the hot exciton-magnon combination band (i.e., the hot magnon sideband, called the hot band hereafter) in 1D ferromagnets. A different temperature (T) dependence has been observed between the hot band of $CsNiF_3$ and those of $CsFeCl_3$ and $RbFeCl_3$. The former hot band grows in proportion to T at low temperatures,[5] in agreement with the theory of Ebara and Tanabe.[9] On the other hand, the hot-band intensity of $CsFeCl_3$ and $RbFeCl_3$ deviates from the theoretical curve since the intensity does not decrease toward zero as the temperature approaches 0 K.[2,8,10] Krausz, Viney, and Day[2] have suggested that the zero-point fluctuations of the spin system are responsible for the residual intensity at 0 K, whereas Bontemps, Grisolia, Nozzi, and Briat[8] and Tsuboi, Chiba, and Ajiro[7] have suggested that the observed bands do not consist only of the hot bands but that they contain additional T-independent non-hot bands such as the exciton and cold bands. The present investigation was undertaken to clarify the origin of the residual intensity observed in $CsFeCl_3$.

Another reason why $CsFeCl_3$ was chosen for the present investigation is that it is an unusual ferromagnet where (1) the ground state is a singlet state,[6,11,12] and (2) unlike in the case of $RbFeCl_3$,[1,2,11,13] no long-range order appears because of a ferromagnetic exchange interaction J smaller than the energy gap D between the singlet ground state and the doublet excited state,[11] but (3) 3D long-range order is observed to appear when an external magnetic field is applied along the c axis.[13,14] It is interesting to investigate the magnetism of such a 1D ferromagnet with the nonmagnetic ground state. For example, it is important to know how much the magnetic moment is induced in the singlet state by the exchange interaction.

$CsFeCl_3$ is an easy-plane system, the spins lying perpendicular to the c axis. Thus, if the external magnetic field is applied along the easy plane, spin fluctuation is reduced and we expect a big change in the hot bands. This will help to clarify the absorption bands in question. Therefore, in this paper, we examine the behavior of the absorption spectrum under a transverse field.

II. EXPERIMENTAL PROCEDURE AND RESULTS

The single crystal of $CsFeCl_3$ was cut along the c axis and cooled in a glass cryostat which allows cooling down to 1.5 K. The pulsed magnet at the High Magnetic Field Laboratory, Osaka University, was used to apply a magnetic field H_0 perpendicular to the c axis of the crystal. An EG&G model No. FX-132 Xe flash lamp was used as

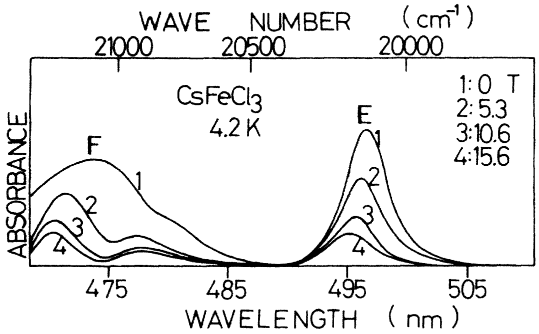

FIG. 1. Absorption spectra, measured at 4.2 K, of $CsFeCl_3$ in the E-F band region at various magnetic fields.

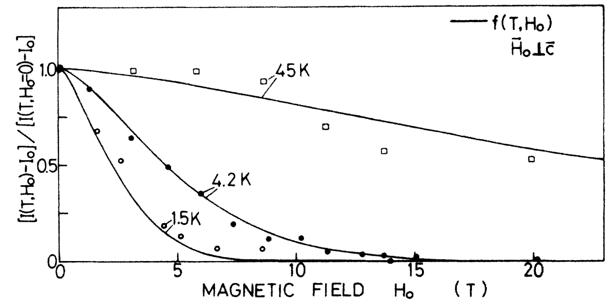

FIG. 2. The E-band absorption intensity, which was subtracted from the constant value I_0 obtained at high fields, plotted against the magnetic field. The continuous line is the curve of $f(T,H_0)$ function in Eq. (4) (see text).

a light source. The light transmitted through the sample was detected by a Princeton Applied Research model No. OMA-2 optical multichannel analyzer attached to a Ricoh-Tusho MC-20 monochromator. The details of the experimental method are described in Ref. 15.

Figure 1 shows the absorption spectra of $\mathrm{CsFeCl_3}$ in the 470–510-nm region at various magnetic fields. In this region there appear two absorption bands called the E and F bands.[7] Here, we discuss only the E band. As the field is increased, the E band is found to decrease in intensity (Fig. 2) and to shift position towards the high-energy side (Fig. 3). The intensity decrease, however, stops at high fields. As indicated in Fig. 2, a constant value I_0 is obtained at high fields at both 1.5 and 4.2 K. It is noted that the I_0 value is almost the same for 1.5 and 4.2 K, and furthermore, the I_0 value is reached at lower field at 1.5 K than at 4.2 K, i.e., the intensity decrease becomes slower as the temperature is raised. Our data are consistent with the result of Krausz *et al.*[2] who measured the E-band intensity at a magnetic field of 5 T.

III. OPTICAL TRANSITIONS IN THE SINGLET-GROUND-STATE FERROMAGNET

In an octahedral or cubic field, the ^5D ground state of the $\mathrm{Fe^{2+}}$ ion (d^6 electron configuration) is split into a lower $^5T_{2g}$ level and an upper ^5E_g level. The ground $^5T_{2g}$ level is split into the effective total angular momentum components $J'=1,2,3$ by the spin-orbit interaction. The lowest $J'=1$ state is further split into a low-lying singlet state ($J_z'=0$) and an upper doublet state ($J_z'=\pm 1$) by the trigonal crystal field.[2,12,16] The perturbation by the exchange interaction between two $\mathrm{Fe^{2+}}$ ions gives rise to level mixing between the nonmagnetic singlet ground state and the upper doublet state. The effective spin Hamiltonian for the ground state with fictitious spin $S=1$ (instead of $J'=1$) is written as[11,16]

$$\mathcal{H} = -2J\sum_i \mathbf{S}_i\cdot\mathbf{S}_{i+1} + D\sum_i (S_i^z)^2 - \sum_i g\mu_B \mathbf{H}_0\cdot\mathbf{S}_i \ , \qquad (1)$$

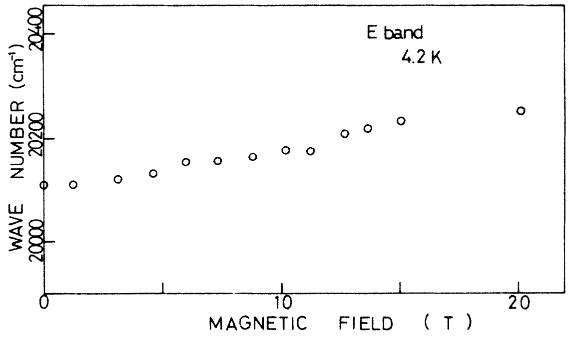

FIG. 3. Peak position, measured at 4.2 K, of the E band plotted against the transverse field.

where D, μ_B, and g are the uniaxial anisotropy constant, the Bohr magneton, and the g value, respectively. The g value was estimated as $g_\parallel=2.5$ by Steiner *et al.*[12] but the value of $g_\perp$ is unknown. The experimental values of J and D so far reported are scattered.[11,12,16] Yoshizawa, Kozukue, and Hirakawa obtained $J=1.83\ \mathrm{cm^{-1}}$ and $D=17.58\ \mathrm{cm^{-1}}$ by neutron scattering measurements.[11] Their values are used in this paper.

When the external magnetic field $\mathbf{H}_0$ is applied perpendicular to the c axis (z axis), the direction of the exchange field $\mathbf{H}^*$ is parallel to the applied field because of the easy-plane anisotropy. In this case, the exchange and Zeeman terms of Eq. (1) are combined and expressed approximately as $g_\perp \mu_B S H_{\mathrm{eff}}$, where $H_{\mathrm{eff}}=H_0+H^*$. In Fig. 4 we show the $S=1$ energy levels under the effective field H_{eff}. In Fig. 4 we assumed $g_\perp = g_\parallel$ ($=2.5$) since in $\mathrm{RbFeCl_3}$ the two g values are quite close to each other.[17] As seen in this figure, the doublet state is split into two levels, the separation between the ground level (level 1) and the lowest excited level (level 2) is given by

$$W_{21} = D/2 + [(D/2)^2 + (g_\perp \mu_B H_{\mathrm{eff}})^2]^{1/2} \ . \qquad (2)$$

The magnon sideband is induced by the spin-dependent electric dipole transition moment $\mathbf{P}_{jl}$. The $\mathbf{P}_{jl}$ is written as

$$\mathbf{P}_{jl} = \Pi(j^*l)\sigma_j\cdot\mathbf{S}_l \ , \qquad (3)$$

where σ_j is a pseudospin operator which acts on the J_z spin component of the j-site ion when the j ion is excited from the ground state to the spin-forbidden excited state, and $\mathbf{S}_l$ is a spin operator acting on the ground state of the

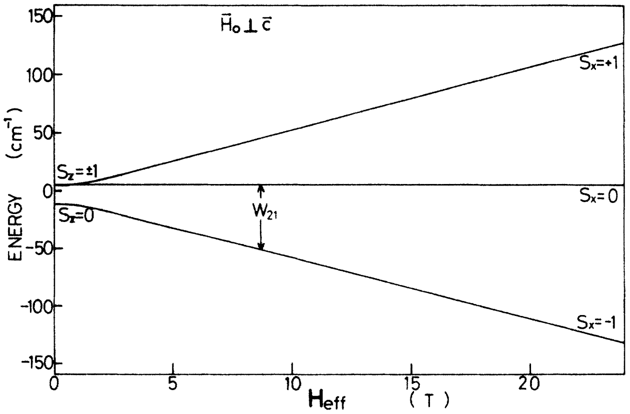

FIG. 4. Level splitting of the $\mathrm{Fe^{2+}}$ ground state with fictitious spin $S=1$ under the effective field H_{eff}.

neighboring l-site ion.[8,18] Such a spin-dependent transition moment induces the exciton-magnon transition where an exciton is created at the j-site ions while a magnon is created or annihilated at the l-site ions. Equation (3) leads to the selection rule that the total spin component should be conserved in the transitions. Here we consider the sideband associated with an exciton transition from the fictitious spin $S=1$ ground state $|S=1,S_z=0,\pm 1\rangle$ to the excited state $|S',S_z'\rangle$. It is easily shown that the $\sigma_j \cdot \mathbf{S}_l$ term[18] allows only the hot band for the transition to the $S'=0$ state [see Fig. 5(a)], whereas it allows both the cold band seen in Fig. 5(b) and the hot band seen in Fig. 5(c) for the transition to the $S'=2$ state. That is to say, the transition shown in Fig. 5(b) is allowed because of nonvanishing matrix element $\sigma_{j+}S_{l-}$. The difference between the hot and cold bands is obvious: The cold band is allowed even at 0 K and its intensity is almost T independent, whereas the hot band is not allowed at 0 K and its intensity increases with increasing temperature.

The E band is assigned to the absorption associated with the electronic transition ${}^5T_{2g} \rightarrow {}^3T_{1g}$ of the Fe^{2+} ion.[7] We can use the fictitious spin $S'=0,1,2$ for the ${}^3T_{1g}$ levels with the ${}^5T_{2g}$ ground state. This suggests that the exciton-magnon transition associated with the ${}^5T_{2g} \rightarrow {}^3T_{1g}$ electronic transition gives rise to both the cold and hot bands. The E band is certainly observed to have a strong absorption intensity even at 1.5 K although its intensity is reduced with decreasing temperature; the residual intensity near 0 K is understood to arise from the cold band.

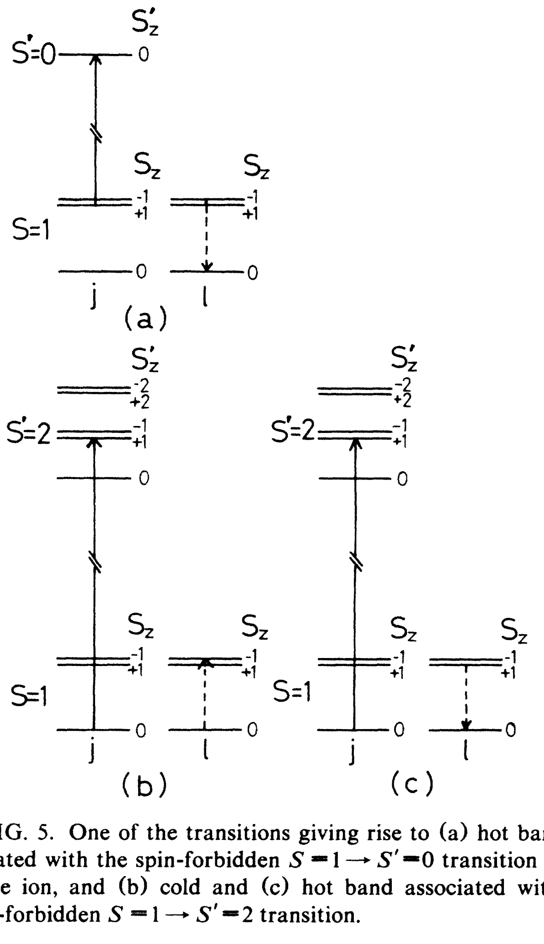

FIG. 5. One of the transitions giving rise to (a) hot band associated with the spin-forbidden $S=1 \rightarrow S'=0$ transition in the j-site ion, and (b) cold and (c) hot band associated with the spin-forbidden $S=1 \rightarrow S'=2$ transition.

IV. DISCUSSION

When the magnetic field is applied perpendicular to the c axis (z axis), the intensity of the hot band decreases with increasing field because the separation W_{21} between the lowest excited state and the ground state increases with the field, giving rise to a decrease of the thermal population of the excited state which is responsible for the hot band. The thermal population can be assumed to be proportional to $\exp(-W_{21}/kT)$. Therefore, it is expected that the hot-band intensity decreases exponentially with increasing field. It, however, never vanishes, even at high fields as seen in Fig. 1; the residual intensity I_0 is the same between 1.5 and 4.2 K. We assume that the E-band intensity $I(T,H_0)$ is expressed by

$$I(T,H_0)=a(T)f(T,H_0)+I_0\,, \tag{4}$$

where the first term comes from the hot-band intensity. The thermal population of the lowest excited state $f(T,H_0)$ is normalized to $f(T,H_0=0)=1$;

$$f(T,H_0)=\exp[([(D/2)^2+(g_\perp \mu_B H^*)^2]^{1/2} \\ -\{(D/2)^2+[g_\perp \mu_B (H_0+H^*)]^2\}^{1/2})/kT]\ . \tag{5}$$

Therefore $a(T)$ is the hot-band intensity at $H_0=0$.

To check the validity of Eq. (4), we compare $f(T,H_0)$ with the experimental value of $[I(T,H_0)-I_0]/[I(T,H_0=0)-I_0]$. As seen in Fig. 2, the experimental data fit the $f(T,H_0)$ curve quite well, not only at 1.5 and 4.2 K, but also at 45 K. The good fit was obtained when we assumed $H^*=1$ T for the exchange-field appearing in Eq. (5). This indicates that the E band consists of the H_0- and T-dependent hot band and a H_0- and T-independent band. The best candidate for the origin of the latter band is the cold band since the E band contains the cold band at zero field as mentioned above.

We can show the presence of the cold band even at high field as follows. When the magnetic field is applied along the x axis and the field is considerably strong, the ground-state wave functions are modified by the level mixing of the ground state with the lowest excited doublet. We can take the x axis as a new quantization axis since the field is parallel to the x axis. The ground state is therefore characterized by the spin state $S_x=-1$ at high field as shown in Fig. 4. Similar level mixing is also caused in the excited ${}^3T_{1g}$ state. It is easily shown that such a new level diagram at high field also allows the appearance of a cold band associated with the spin-forbidden $S=1 \rightarrow S'=2$ transition.

The singlet ground state of Fe^{2+} ion in $CsFeCl_3$ gives expectation values of spin $\langle S \rangle=0$ and its z component $\langle S_z \rangle=0$ in zero exchange interaction and zero magnetic field, i.e., the level is nonmagnetic. The magnetic moment, however, is induced to the ground state by the exchange interaction through level mixing with the upper doublet state. The induced magnetic moment is calculated from the exchange field H^*. We obtained $H^* = 1$ T as mentioned above. Therefore, using the values of $J = 1.83$ cm^{-1} and $g_\perp = 2.5$, we obtain $\langle S \rangle = 0.16$ for the 1D ferromagnet $CsFeCl_3$. This value is too small when compared with the theoretical saturation value of the magnetic moment, $2.5\mu_B$. Such a small $\langle S \rangle$ value is consistent with the fact that the exchange constant J is smaller than the anisotropy constant D ($J/D \sim 0.1$) which gives the separation between the singlet and doublet levels.

V. CONCLUSION

It has been suggested and confirmed for a long time that both the hot and cold bands are allowed in antiferromagnets, but only the hot band is allowed in ferromagnets.[8,19] From the magnetic field effect on the absorption bands in $CsFeCl_3$ and its analysis, however, we found that the cold band is also allowed in the 1D ferromagnet. That is, the E band of $CsFeCl_3$ was found to consist of not only the field- and temperature-dependent hot band but also the field- and temperature-independent cold band. The present analysis indicates that the appearance of the cold band in $CsFeCl_3$ is predominantly due to the much stronger spin-orbit interaction and trigonal crystal field for the single Fe^{2+} ion than the exchange interaction between Fe^{2+} ions, which gives rise to the singlet gound state. Moreover, the present analysis indicates that the exchange-field model is useful to explain the field dependence of the E band.

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