Cr³⁺ EXCITON MOTION IN RARE EARTH ORTHOCHROMITE RCrO₃

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ABSTRACT

We have investigated the optical absorption spectra corresponding to the $4A_{2g} \rightarrow 2E_g$ transition of Cr³⁺ in various rare earth orthochromites RCrO₃. In the case that the R³⁺ ion is magnetic, an electric dipole band (R' band) was observed in the neighborhood of the Cr³⁺ exciton lines. The R' bands were classified into three groups on the basis of their behaviors as follows: (1) The R' band in RCrO₃ (R=Yb and Tm) are the combined excitation of a Cr³⁺ exciton and a R³⁺ spin flip which is induced by the anisotropic parts of the Cr³⁺-R³⁺ exchange interaction. (2) The R' band in GdCrO₃ is the combined excitation of a Cr³⁺ exciton and a R³⁺ spin flip which is induced by the isotropic part of the Cr³⁺-R³⁺ exchange interaction. (3) The R' band in RCrO₃ (R=Er, Ho, Dy and Tb) is the localized Cr³⁺ exciton which is caused by the R³⁺ spin fluctuation or by the static disorder of the R³⁺ spin configuration. From the analysis of the R' band, it was elucidated that the Cr³⁺-R³⁺ magnetic interaction plays an important role in the Cr³⁺ exciton motion in RCrO₃.

1. INTRODUCTION

It is well known that the rare earth orthochromites RCrO₃, as well as the rare earth orthoferrites RFeO₃, show interesting magnetic properties such as spin reorientation induced by the temperature and magnetic field. In RCrO₃, there are three types of magnetic interaction, Cr³⁺-Cr³⁺, Cr³⁺-R³⁺ and R³⁺-R³⁺, each of which generally consists of the isotropic, and the anisotropic symmetric and antisymmetric exchange interactions. Yamaguchi have shown that the anisotropic parts of the Cr³⁺-R³⁺ exchange interaction are generally responsible for the spin reorientation.[1]

The magneto-optical properties of RCrO₃ have been extensively investigated during the past fifteen years. Aoyagi, Tsushima and Sugano[2] first reported the observation of Davydov splitting in the R exciton lines corresponding to the $4A_{2g} \rightarrow 2E_g$ transition in YCrO₃. And, detailed analyses of the R exciton lines in RCrO₃ have been performed by Melzer,[3] and Sugano, Aoyagi and Tsushima.[4] In their works, they have exposed symmetry properties and dispersion relations of the R excitons, in terms of matrix elements of excitation transfer between Cr³⁺ ions in the crystal. It has been shown that the observed polarization properties of the R exciton lines agree with the selection rule theoretically obtained, and the magnetic symmetry change associated with spin reorientation is directly reflected in the selection rule of the polarized R exciton lines.

Recently, in the neighborhood of the R exciton lines, a satellite band (R') of electric dipole origin has been observed in several rare earth orthochromites.[5-9] On the other hand, in the case that the R³⁺ ion is a non-magnetic ion such as Lu³⁺ etc., the R' band has not been observed.[2,9] The behavior of the R' band remarkably depends on the kind of the rare earth ion.

In the present paper, the R' bands are classified on the basis of their behaviors. With regard to this, we discuss the relation between the characteristic properties of the R³⁺ ion and the behavior of the R' band, and elucidate the reason why the transition mechanism of the R' band in RCrO₃ depends on the kind of the R³⁺ ion. And, from the analysis of the R' band, we discuss the influence of the Cr³⁺-R³⁺ magnetic interaction on the Cr³⁺ exciton motion in RCrO₃.

We briefly summarize important properties of RCrO₃. The crystal has an orthorhombically distorted perovskite structure

Fig.1 Unit cell of RCrO₃. The Cr³⁺ and R³⁺ positions are indicated with numbers 1-4 and 5-8, respectively.

Fig.2 Spin configurations of RCrO₃ at T_{N2} < T < T_{N1}. [11]

belonging to the space group $P6_3mm(D_{2h}^{16})$. [10] The unit cell of $R\text{CrO}_3$ contains four molecules as shown in Fig.1. The Cr^{3+} spins order spontaneously at Néel temperature T_{N1} and these compounds generally exhibit a weak ferromagnetic moment. And at the second Néel temperature T_{N2} , the R^{3+} spins begin to reorder antiferromagnetically. The allowed spin configurations for the Cr^{3+} and R^{3+} sites at $T_{N2} < T < T_{N1}$ are shown in Fig.2.

2. EXPERIMENTAL RESULTS

Fig.3 shows the absorption spectra in the lowest energy region of the $4A_{2g} \rightarrow 2E_g$ transition of Cr^{3+} in various rare-earth orthochromites. In this energy region, four magnetic dipole lines (R_1, R_2, R_3 and R_4) and an electric dipole band (R') are observed. The R_1 — R_4 lines are Davydov-split components of the Cr^{3+} exciton corresponding to the transition from the lowest substate of $4A_{2g}$ to the lowest substate of $2E_g$ of the Cr^{3+} ion, [4] which is schematically shown in Fig.4. As shown in Fig.3, the R' band in $R\text{CrO}_3$ ($R=\text{Yb}$ and Tm) lies on the higher energy side of the R exciton lines and it has an anomalous shape with several peaks. On the other hand, the R' band in $R\text{CrO}_3$ ($R=\text{Er}, \text{Ho}, \text{Dy}, \text{Tb}$ and Gd) lies on the lower energy side of the R exciton lines, and it comprises a single peak.

The R' bands in these orthochromites can be classified into three groups on the basis of their behaviors.

2-1 R' band in $R\text{CrO}_3$ ($R=\text{Yb}$ and Tm)

The R' band in $R\text{CrO}_3$ ($R=\text{Yb}$ and Tm) lies on the higher energy side of the R exciton lines, which has an anomalous shape with several peaks. Its intensity does not appreciably depend on temperature.

Fig.5 shows the behaviors of the R exciton lines and the R' bands in $R\text{CrO}_3$ ($R=\text{Yb}$ and Tm) under the external magnetic field parallel to the direction of the net R^{3+} magnetic moment. The magnetic field dependences of the energy positions of the R exciton lines and the R' band in YbCrO_3 are very similar to those in TmCrO_3 . In both compounds, when the magnetic field is applied along the direction of the net R^{3+} magnetic moment, the energies of R exciton lines shift slightly to the higher energy side and then remain unchanged. On the other hand, the peaks of the R' band shifts always to the higher energy side with increasing magnetic field.

In the case of YbCrO_3 , in the range of magnetic fields where the energies of R exciton lines remain unchanged, the linear shift of R' band takes place, which is almost equal to the field induced splitting of the Yb^{3+} ground Kramers doublet. [12] Therefore, it is concluded that the R' band in YbCrO_3 is the combined excitation of a Cr^{3+} exciton and a Yb^{3+} spin flip.

As already mentioned in previous paper, [12] the splitting of the Yb^{3+} ground Kramers doublet is 21.3cm^{-1} at 4.2K , while the R' band lies at the spectral position about $5\sim 35\text{cm}^{-1}$ higher than the average energy of the R exciton lines and its lowest energy side is sharply cut off. These properties of the R' band imply that the energy of the R exciton at the Brillouin-zone boundary is considerably lower than that of the exciton at the zone center. That is to say, the R exciton has a large negative dispersion, which is caused by the intra-sublattice exciton transfer.

The exciton dispersion due to the spin allowed transfer is expressed as;*

$$E(k) = E_0 + 2V_{11}^a \cos(ak_x) + 2V_{11}^b \cos(bk_y) + 8V_{13} \cos(ak_x/2) \cos(bk_y/2) \cos(ck_z/2), \quad (1)$$

* In order to simplify the calculation, the spin forbidden inter-sublattice transfer (V_{12} and V_{14}) are neglected.

Fig.3 Absorption spectra in the lowest energy region of the $4A_{2g} \rightarrow 2E_g$ transition of Cr^{3+} in various rare-earth orthochromites. H and E denote the magnetic and electric vectors of the incident light, respectively.

Fig.4 Davydov-split $k=0$ exciton states corresponding to the transition from the $4A_{2g}$ state to the $2E_g$ state of the Cr^{3+} ion in $R\text{CrO}_3$

Fig.5 Magnetic field dependence of the energies of R exciton lines and R' bands in YbCrO₃ and TmCrO₃. In the case of TmCrO₃, the energy position of R_I' is taken as the center of the R_I'-1 and R_I'-4 peaks, and that of R_{II}' is taken as the center of the R_{II}'-1 and R_{II}'-2 peaks.

Fig.6 Energy dispersion of the Cr³⁺ exciton due to the spin-allowed exciton transfers, where $V_{11}^a = 3.0 \text{ cm}^{-1}$, $V_{11}^b = 1.0 \text{ cm}^{-1}$ and $|V_{13}| = 0.13 \text{ cm}^{-1}$.

Fig.7 Temperature dependence of the energy position and the integrated intensity of the R' band in GdCrO₃.

where E_0 is the relevant excitation energy for the single Cr³⁺ ion, and V_{ij} represents the exciton transfer between the i - j Cr³⁺ pair (i and j label the inequivalent Cr³⁺ sites in a unit cell). To be more specific, V_{11}^a and V_{11}^b represent the intra-sublattice transfers along the a - and b -axes, respectively, and V_{13} the spin allowed inter-sublattice one, which has been estimated to be 0.13 cm^{-1} . [8] According to eq.(1), the energy difference between the exciton at the zone boundary (R and S symmetry points) and that at the zone center (Γ point) is given by $-4(V_{11}^a + V_{11}^b)$.

When the magnitude of the intra-sublattice exciton transfer is adequately taken into account, several peaks and cut-off profile on the lowest energy side appear in the joint density of states of the Cr³⁺ exciton-Yb³⁺ spin flip. By setting $-4(V_{11}^a + V_{11}^b) = -16 \text{ cm}^{-1}$, the energy position, band width and the cut-off profile at the lowest energy side of the R' band in YbCrO₃ could be reproduced in computer simulation. [8] The appearance of the multiple peaks in the R' band may be attributed to the Van Hove singularities in the density of exciton states. The energy dispersion of the R exciton in YbCrO₃ is shown in Fig.6.

In the same way, the R_I' band in TmCrO₃ is considered to be the combined excitation of a Cr³⁺ exciton and the transition from the ground state to the lowest excited crystal field state (17.7 cm^{-1}), and the R_{II}' band is the combined excitation of a Cr³⁺ exciton and the transition from the ground state to the second lowest excited crystal field state (41.3 cm^{-1}) of Tm³⁺. From the analysis of the R_I' and R_{II}' bands, the negative dispersion of the R exciton in TmCrO₃ is estimated to be -14 cm^{-1} .

In conclusion, the R' band in RCrO₃ (R=Yb and Tm) is the combined excitation of a Cr³⁺ exciton and a R³⁺ spin flip, which is induced by the anisotropic parts of the Cr³⁺-R³⁺ exchange interaction, because the direction of the R³⁺ sublattice magnetic moment is perpendicular to that of the Cr³⁺ sublattice magnetic moment.

2-2 R' band in GdCrO₃

The R' band in GdCrO₃ lies on the lower energy side of the R exciton band, whose band width is broad. Fig.7(a) shows the temperature dependence of the energy position of the R' band. The energy position of the R' band shifts to the lower energy side with increasing temperature from 1.5 K and a relatively steep drop of energy occurs at about $T_{N2} (= 2.42 \text{ K})$, and then it remains unchanged from T_{N2} to 4.2 K. Fig.7(b) shows the temperature dependence of the integrated intensity of the R' band. When the temperature is increased from 1.5 K, the intensity of the R' band decreases abruptly in the range of 1.5 K to T_{N2} , and above T_{N2} it decreases slightly.

The behaviors of the energy position and the intensity of the R' band at T_{N2} resemble closely those of the cold band of the magnon sideband at the Néel temperature in magnetic insulators, and which suggests that the R' band in GdCrO₃ is the combined excitation of a Cr³⁺ exciton and a Gd³⁺ spin flip. The energy shift (3.5 cm^{-1}) of the R' band at temperatures from 1.5 K to T_{N2} is considered to be due to the exchange splitting of the Gd³⁺ ground state induced by the Gd³⁺-Gd³⁺ exchange interaction. On the other hand, Cooke et al. [13] have estimated the splitting of the Gd³⁺ ground state induced by the Cr³⁺-Gd³⁺ interaction to be 0.5 cm^{-1} , from the magnetization measurement. Therefore, the spin flip energy of the Gd³⁺ ion induced by the Gd³⁺-Gd³⁺ and the Cr³⁺-Gd³⁺ interactions is estimated to be less than 4 cm^{-1} . Therefore, the band width (20 cm^{-1}) of the R' band is mostly responsible for the exciton dispersion. Since the R exciton band lies at the higher energy side of the R' band, the sign of the Cr³⁺ exciton dispersion is considered to be negative, which is

similar to that of the Cr^{3+} exciton dispersion in RCrO_3 ($\text{R}=\text{Yb}$ and Tm).

By the way, the antisymmetric and the anisotropic-exchange interactions between the orbitally non-degenerate ions such as Gd^{3+} and Cr^{3+} ions are one and two orders of magnitudes smaller than the corresponding isotropic exchange interaction, respectively. So that, the R' band in GdCrO_3 must be induced by the isotropic exchange interaction between the Gd^{3+} and Cr^{3+} ions.

In fact, the behavior of the R' band in GdCrO_3 can be explained by this transition mechanism as follows; Below $T_{\text{N}2}$, the Gd^{3+} spins are antiferromagnetically ordered and its antiferromagnetic axis is almost parallel to that of the Cr^{3+} spins. Therefore, the Cr^{3+} - Gd^{3+} isotropic exchange interaction effectively induces the appearance of the R' band. While, when the magnetic field is applied along any of the three crystal axes at $T < T_{\text{N}2}$, the magnetic moment due to the Gd^{3+} spins saturates and its direction becomes perpendicular to that of the Cr^{3+} spins at $H_0 \geq 20\text{kOe}$, where the Cr^{3+} - Gd^{3+} isotropic exchange interaction loses its effect, therefore the intensity of the R' band becomes nearly zero in this magnetic field region. [9]

In conclusion, the R' band in GdCrO_3 is the combined excitation of a Cr^{3+} exciton and a Gd^{3+} spin flip, which is induced by the isotropic part of the Cr^{3+} - Gd^{3+} exchange interaction.

2-3 R' band in RCrO_3 ($\text{R}=\text{Er}$, Ho , Dy and Tb)

The R' band in RCrO_3 ($\text{R}=\text{Er}$, Ho , Dy and Tb) lies at the spectral position about 15cm^{-1} lower than the R exciton lines, which comprises a single peak. The intensity of R' is most conspicuous in the $E//a$ polarization, and has a strong temperature dependence.

Fig.8 shows the behaviors of the R exciton lines and the R' band in RCrO_3 ($\text{R}=\text{Er}$, Ho , Dy and Tb) under the magnetic field along the direction of the net R^{3+} magnetic moment at $T > T_{\text{N}2}$. When the magnetic moment of the R^{3+} spins approaches saturation with increasing external magnetic field, the intensity of the R' band becomes weak and then disappears.

The energy positions of the R exciton lines and the R' band almost remain unchanged with increasing magnetic field. Concerning with the R^{3+} ground state, the R^{3+} spin-flip energy becomes large with increasing magnetic field. For example, when the magnetic field parallel to the direction of the R^{3+} magnetic moment is applied up to 25.0kOe , the increments of the R^{3+} spin-flip energy for ErCrO_3 , HoCrO_3 , DyCrO_3 and TbCrO_3 are 14.1cm^{-1} , 8.2cm^{-1} , 6.5cm^{-1} and 8.3cm^{-1} , respectively. [9]

Therefore, the field induced energy shift of the R' band in RCrO_3 ($\text{R}=\text{Er}$, Ho , Dy and Tb) disagrees with the sum of the energy shift of the R exciton and the field induced increment of the R^{3+} spin-flip energy, which implies that the R^{3+} spin-flip is not comprised in the transition responsible for the R' band in RCrO_3 ($\text{R}=\text{Er}$, Ho , Dy and Tb).

In what follows, some remarkable behaviors of the R' band under magnetic fields, and from which we will make clear the transition mechanism of the R' band in RCrO_3 ($\text{R}=\text{Er}$, Ho , Dy and Tb).

Fig.9 shows the behavior of the R' band in HoCrO_3 in the magnetic field $H_0//b$ at 1.5K . At 1.5K , the R' band could not be found. While, when the magnetic field is applied along the b -axis, the R' band appears at about 10kOe , and its intensity passes through a maximum which lies at about 16kOe , and then decreases. Now, we investigate the reason why the intensity of the R' band in HoCrO_3 has a maximum at $H_0(//b)=16\text{kOe}$.

In HoCrO_3 , the Cr^{3+} sublattice magnetic moments and the Cr^{3+} net magnetic moment lie along the c - and a -axes, respectively. The anisotropy axes of the Ho^{3+} ions lie in the a - b plane at about $\pm 65^\circ$ from the a -axis, [14] and the g -value parallel to the anisotropy axis is 17.3 and that perpendicular to the anisotropy axis is negligibly small. [15] Therefore, the Ho^{3+} spins are strictly confined to these two anisotropy axes. From the behavior of the $^5\text{I}_8 \rightarrow ^5\text{S}_2$ transition of Ho^{3+} in the magnetic field $H_0//b$, we can determine the spin configurations of HoCrO_3 in various magnetic fields, which is shown in Fig.10. [16] As shown in Fig.10, when the magnetic field is increased along the b -axis, the sublattice magnetic moments M_j^{Ho} due to the S_7^{Ho} and S_8^{Ho} spins decrease and vanish at about 16kOe , and above 16kOe they grow gradually toward the direction of the applied magnetic field. On the other hand, $M_{j=5,6}^{\text{Ho}}$ are saturated in the whole field range.

From the behavior of the R' band and the spin configuration of HoCrO_3 in the magnetic field $H_0//b$,

Fig.8 Behavior of the R' band in the magnetic field at $T > T_{\text{N}2}$ in RCrO_3 ($\text{R}=\text{Er}$, Ho , Dy and Tb). The magnetic field is applied along the direction of the weak ferromagnetic moment.

Fig.9 Magnetic field dependence of the intensity of the R' band at 1.5K in HoCrO_3 . The magnetic field $H_0//b$.

Fig.10 Spin configurations of HoCrO_3 in various magnetic fields at 1.5K. The magnetic field $H_0 \parallel b$. $M_{i=1-4}^{\text{Cr}}$ and $M_{j=5-8}^{\text{Ho}}$ denote the sublattice magnetic moments due to the $S_{i=1-4}^{\text{Cr}}$ and $S_{j=5-8}^{\text{Ho}}$ spins, respectively.

one arrives at the conclusion that when the magnetic field is applied along the b-axis, the Ho^{3+} spins (S_7^{Ho} and S_8^{Ho}) fall into disorder at about 16kOe, where the intensity of the R' band increases abruptly. In conclusion, the transition responsible for the R' band in HoCrO_3 is allowed when the Ho^{3+} spins are fluctuated by temperature or external magnetic field.

Similar behavior of the R' band has been observed in DyCrO_3 by Aoyagi et al.[7] Fig.11 shows the behavior of the R' band in the magnetic field $H_0 \parallel a$ at $1.5\text{K} < T_{N2}$ in DyCrO_3 . When the magnetic field is applied along the a-axis, the intensity of the R' band increases abruptly at 2~3kOe and then decreases in the field region between 4kOe and 8kOe. At about 12~13kOe its intensity increases abruptly again, and then decreases and becomes nearly zero at about 20kOe.

It is well known that, below T_{N2} the magnetization along the a-axis in DyCrO_3 increases stepwise at two values of magnetic field and that the magnetization after the first step is a half of that of the final state.[17] This stepped magnetization process is attributed to the change of the Dy^{3+} spin configuration. At about 3 and 14kOe, the magnetic moments due to the S_6^{Dy} and D_8^{Dy} spins are going to reverse their directions from being antiparallel to parallel to the external magnetic field, and where the intensity of the R' band abruptly becomes large. In the vicinity of the magnetic fields (3kOe, 14kOe), magnetic domains due to the coexistence of the two kinds of the Dy^{3+} spin configurations appear, and which should be responsible for the abrupt increase of the intensity of the R' band at about 3 and 13kOe.

In conclusion, the transition responsible for the R' band in DyCrO_3 is allowed when the Dy^{3+} spins are fluctuated at finite temperature or magnetic domains of the Dy^{3+} spin configuration exist below T_{N2} .

In the case of TbCrO_3 , below T_{N2} ($=3.05\text{K}$) the antiferromagnetic order of the Tb^{3+} spins is formed in an enlarged magnetic unit cell (a, 2b, c) by the Tb^{3+} - Tb^{3+} magnetic dipole interaction.[18] In this phase, stacking faults of the Tb^{3+} spin configuration occur. This magnetic stacking faults are annealed with the magnetic field of about 6kOe along the a-axis,[19] where the R' band disappears completely as shown in Fig.12. Thus, it is obvious that the existence of the stacking faults of the Tb^{3+} spin configuration is responsible for the appearance of the R' band in TbCrO_3 .

In what follows, the characteristic properties of the R' band in RCrO_3 ($R=\text{Er, Ho, Dy and Tb}$) are summarized as follows; (1) The R' band comprises a single peak. It lies at the spectral position about 15cm^{-1} lower than the average energy of the R exciton lines. (2) The dipole nature of the R' band is electric, while those of the R exciton lines are magnetic. (3) The field induced energy shift of the R' band disagrees with the sum of the energy shift of the R exciton and the field induced splitting of the R^{3+} ground doublet, which implies that the transition of the R' band does not accompany the R^{3+} spin flip. (4) As the magnetic moment of the R^{3+} spins approaching saturation, the intensity of the R' band becomes nearly zero. (5) The transition responsible for the R' band is allowed when the R^{3+} spins are fluctuated by temperature or external magnetic field. (6) In the case of DyCrO_3 , below T_{N2} a remarkable increase of the intensity of the R' band is caused by the appearance of the magnetic domains due to the coexistence of the different spin configurations of Dy^{3+} . In the case of TbCrO_3 , a remarkable increase of the intensity of the R' band below T_{N2} is caused by the appearance of the magnetic stacking faults of the Tb^{3+} spin configuration.

From these experimental results, one arrives at the conclusion that the R' band in RCrO_3 ($R=\text{Er, Ho, Dy and Tb}$) is the bound Cr^{3+} exciton trapped by the deformed potential due to the fluctuation of the R^{3+} spins or the static disorder (i.e. magnetic domains) of the R^{3+} spin configuration.

Fig.11 Magnetic field dependence of the intensity of the R' band at 1.5K in DyCrO_3 . The magnetic field $H_0 \parallel a$.

Fig.12 Magnetic field dependence of the intensity of the R' band at 1.5K in TbCrO_3 . The magnetic field $H_0 \parallel a$.

In order to make clear the origin of the R' band, it will be indispensable to take into account that the disorder of the R^{3+} spin configuration deforms effectively the periodic lattice potential through the medium of the magneto-elastic effect. This deformed potential will presumably bind the Cr^{3+} exciton, and whose spectrum appears as R' band lying on the lower energy side of the free exciton lines (R lines). Strange to say, the energy position of the R' band in $RCrO_3$ (R=Er, Ho, Dy and Tb) agrees very closely with that of the Cr^{3+} exciton at the zone boundary.

3. CONCLUSION

We have investigated the optical absorption spectra corresponding to the $^4A_{2g} \rightarrow ^2E_g$ transition of Cr^{3+} in various rare earth orthochromites. In the case that the R^{3+} ion is magnetic, an electric dipole band (R' band) was observed in the neighborhood of the Cr^{3+} exciton lines (R_{1-4}).

The R' bands in $RCrO_3$ are classified into three groups on the basis of their behaviors as follows;

- (1) The R' band in $RCrO_3$ (R=Yb and Tm) is the combined excitation of a Cr^{3+} exciton and a R^{3+} spin flip which is induced by the anisotropic parts (i.e. antisymmetric and anisotropic-symmetric parts) of the Cr^{3+} - R^{3+} exchange interaction.
- (2) The R' band in $GdCrO_3$ is the combined excitation of a Cr^{3+} exciton and a Gd^{3+} spin flip which is induced by the isotropic part of the Cr^{3+} - Gd^{3+} exchange interaction.
- (3) The R' band in $RCrO_3$ (R=Er, Ho, Dy and Tb) is the localized Cr^{3+} exciton bound by the magnetostriction which is caused by the R^{3+} spin fluctuation or by the static disorder (i.e. magnetic domains) of the R^{3+} spin configuration.

As mentioned above, the transition mechanism of the R' band in $RCrO_3$ remarkably depends on the kind of the rare earth ion. From the relation between the characteristic properties of the Cr^{3+} - R^{3+} magnetic interaction and the behavior of the R' band, one arrives at the following conclusion.

If the R^{3+} ion is magnetic, the lattice potential around the R^{3+} ion is deformed by the magneto-elastic effect. When the magnetization of the R^{3+} spins saturates, the lattice potential deformed by the magneto-elastic effect is periodic. So that, the Cr^{3+} exciton can not be bound. However, when the magnetic domains of the R^{3+} spin configuration exist or the R^{3+} spins are fluctuated by temperature or external magnetic field, the disorder of the R^{3+} spin configuration deforms the lattice potential through the medium of the strong magneto-elastic effect, and which binds the Cr^{3+} exciton. This bound Cr^{3+} exciton appears as the R' band in the lower energy side of the free exciton lines (R_{1-4}) in $RCrO_3$ (R=Er, Ho, Dy and Tb).

In the case that the Cr^{3+} - R^{3+} exchange interaction is so strong as those in $YbCrO_3$ and $TmCrO_3$, the Cr^{3+} exciton creates the R^{3+} spin-flip, and this combined quasi-particle migrates on the magnetic ions, and whose spectrum appears as the R' band in the higher energy side of the free exciton lines. Thus, the Cr^{3+} exciton in $RCrO_3$ (R=Yb and Tm) is free from the binding due to the magnetostriction.

In the case of $GdCrO_3$, the R' band induced by the isotropic part of the Cr^{3+} - Gd^{3+} exchange interaction is observed. However, the R' band attributed to the localized Cr^{3+} exciton can not be observed, because the magnetostriction due to the Gd^{3+} spin fluctuation is considered to be too small to bind the Cr^{3+} exciton.

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