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EXCITON LINES IN RARE-EARTH ORTHOCHROMITES

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Abstract. — The exciton lines arising from the Cr$^{3+}$ R-line of the G$\gamma$-type antiferromagnet YCrO$_3$ are studied in magnetic fields up to 50 kOe parallel to the a axis. The polarization of the high field spectrum is consistent with the selection rule for the G$\gamma$-type antiferromagnet, indicating a field-induced spin reorientation from G$_x$ to G$_z$. Other evidences supporting the spin reorientation are also discussed. In DyCrO$_3$ (G$\gamma$-type) four exciton lines are clearly observed when a magnetic field is applied along the b axis. Peculiar properties of these exciton lines are discussed in terms of the antisymmetric Cr$^{3+}$-Dy$^{3+}$ interaction.

Recently optical spectra of antiferromagnetic rare earth orthochromites are being studied by several research groups. In particular, the exciton lines associated with the $t^3_2\,{}^4A_2 \rightarrow t^3_2\,{}^2E$ single-ion excitations have been reported of YCrO$_3$ [1, 2, 3, 4, 5], ErCrO$_3$ [5, 6] and HoCrO$_3$ [5] single crystals in magnetically ordered states. The purpose of the present paper is

1 — to report the behavior of the exciton lines of YCrO$_3$ in high magnetic fields $H_0$ to show a spin reorientation,

2 — to report some peculiar features of the exciton lines and the associated weak band of DyCrO$_3$ in magnetic fields parallel to the b crystal axis to show the importance of the G$\gamma$-type interaction.

The observed behavior of the exciton lines of YCrO$_3$ in magnetic fields up to 50 kOe parallel to the a axis (G$_\gamma$-type after Bertaut's notation [7], $x = a$, $y = b$, $z = c$) is shown in figure 1. In the field range above 40 kOe, two lines are conspicuous with both the $b$- and $c$-polarizations ($H//b$, $c$: $H$ is the oscillating magnetic vector of the incident light). This is consistent with the selection rule for the G$_\gamma$-type spin arrangement: the gradual spin reorientation from G$_x$ to G$_z$ in YCrO$_3$ with the increase of a magnetic field parallel to the a axis has been predicted by Motokawa [8] ($H_0 = 37$ kOe) and is observed by Jacobs, Burne and Levinson ($H_0 = 40 \pm 1$ kOe) in their magnetic measurements. Critical field $H_c$ is defined as the field strength at which the spin reorientation is completed. With the a-polarization two lines are vaguely observed, and one of which coincides with one of the $b$, $c$-polarized lines as indicated in figure 1. At present it is uncertain whether this means the accidental degeneracy of a b, c-polarized exciton line and an a-polarized line or the inapplicability of the selection rule for G$_\gamma$. This point is being examined further.

In our experiment the integrated intensity of the b-polarized lines is found to increase with the increase of a magnetic field: the integrated intensity is given by the intensity of the corresponding single-ion excitation. The observed intensity-increase may be explained if one simply ignores the distortion from the Perovskite structure and assumes the spin reorientation within the a-c plane. To this approximation, however, the integrated intensity of the c-polarized lines should sharply decrease with the increase of a magnetic field in disagreement with the observation. To explain all the observed change of the integrated intensities it would be necessary to take into account the tilting of...
the axes of the CrO₆ octahedron from those of the Perovskite crystal. Some of the points mentioned here has been discussed independently by Meltzer [5].

The field-induced spin reorientation is further evidenced by the behavior of the exciton lines in the low-field range as also noticed by Meltzer [5]. If one ignores the spin reorientation and assumes that the four lines are the Davydov components associated with one single-ion excitation as strongly supported [5] in the case of ErCrO₃, the field-induced shifts of the almost equally spaced lines should be nearly symmetric around the center of the four lines in disagreement with the experiment as shown in figure 2.

The observed big difference in the effective g-values for the upper and lower pairs of the lines may be explained by taking into account the spin reorientation as follows: denoting as \( v_{12} \) and \( v_{14} \), respectively, the matrix elements of the excitation transfer between the nearest-neighbour Cr³⁺ ions in the b-c plane (1-2 pair) and that in the a-b plane (1-4 pair), we first notice that the experimentally determined \( v_{12} \) is much smaller than \( v_{14} \) (\( v_{12} = 0.03 \) cm\(^{-1}\), \( v_{14} = 0.28 \) cm\(^{-1}\)), although the ionic distance in the 1-2 pair is smaller than that in the 1-4 pair. The same situation has also been found [5] in the Gₓ-type ErCrO₃. This unexpected situation can be explained by considering the Aₓ-type [7] spin arrangement compatible with Gₓ: the Aₓ components are antiparallel in the 1-2 pair and parallel in the 1-4. Then, assuming that, in the course of the spin reorientation, the parallel y-component of spins in the 1-2 pair begins to appear and increases, we explain the difference in the effective g-values by introducing the relation,

\[
v_{12}(H_o) = v_{12}(0) + \alpha H_o^2 (\alpha > 0).
\]

It is highly desirable to detect small y-components of spins to justify the present argument.

In DyCrO₃, roughly speaking, two exciton lines are observed in the frequency range, 13 680 ~ 13 690 cm\(^{-1}\), as in YCrO₃. The high frequency line is observed for both the a- and c-polarizations (\( H//a, c \)). The low frequency one is observed for the b-polarization and faint for the c. This is consistent with the selection rule for the Gₓ-type spin arrangement, if two Davydov components with the a- and b-, c-polarizations are assumed to be nearly degenerate. This means that \( v_{12} \) and \( v_{14} \) are very small. By using the same argument as given for YCrO₃, this may be ascribed to the absence (or smallness) of the Gₓ-type [7] component compatible with Gₓ.

The most interesting property of these lines is that they show remarkable shifts or splittings when a magnetic field is applied along the b axis as shown in figure 3. The shifts saturate at a certain value of

\[
\text{Fig. 2. — Frequency shifts of the exciton lines of YCrO₃. The calculated shifts without spin reorientation: --- for } g' = 1.0, \quad \cdots \cdots \text{ for } g' = 3.0 \text{ (} g' \text{; } \text{g-value of the single-ion excited state).}
\]

\[
\text{The observed shifts: } \bullet.
\]

\[
\text{Fig. 3. — Exciton lines and the associated weak band of DyCrO₃ with } H_o//b \text{ at } 4.2 \text{ °K.}
\]

The observed big difference in the effective g-values for the upper and lower pairs of the lines may be explained by taking into account the spin reorientation as follows: denoting as \( v_{12} \) and \( v_{14} \), respectively, the matrix elements of the excitation transfer between the nearest-neighbour Cr³⁺ ions in the b-c plane (1-2 pair) and that in the a-b plane (1-4 pair), we first notice that the experimentally determined \( v_{12} \) is much smaller than \( v_{14} \) (\( v_{12} = 0.03 \) cm\(^{-1}\), \( v_{14} = 0.28 \) cm\(^{-1}\)), although the ionic distance in the 1-2 pair is smaller than that in the 1-4 pair. The same situation has also been found [5] in the Gₓ-type ErCrO₃. This unexpected situation can be explained by considering the Aₓ-type [7] spin arrangement compatible with Gₓ: the Aₓ components are antiparallel in the 1-2 pair and parallel in the 1-4. Then, assuming that, in the course of the spin reorientation, the parallel y-component of spins in the 1-2 pair begins to appear and increases, we explain the difference in the effective g-values by introducing the relation,

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v_{12}(H_o) = v_{12}(0) + \alpha H_o^2 (\alpha > 0).
\]

It is highly desirable to detect small y-components of spins to justify the present argument.

In DyCrO₃, roughly speaking, two exciton lines are observed in the frequency range, 13 680 ~ 13 690 cm\(^{-1}\), as in YCrO₃. The high frequency line is observed for the magnetic field, \( H_o \), which is dependent on temperature. The observed value of \( H_o \) at 1.7 °K is 4 kOe and it is 10 kOe at 4.2 °K, which shows that \( \mu_B H_o/kT \) is constant independent of temperature (\( \mu_B \): Bohr magneton).

Bearing in mind the fact deduced from the Dy³⁺ spectrum in DyCrO₃ that the g-value of the ground Kramers doublet of the Dy³⁺ ions is highly anisotropic (\( g_b \approx 17, g_a < 3, g_c < 1 \)), we speculate that some Dy³⁺-Cr³⁺ interaction is responsible for the observed shifts. In fact the value of \( g_b \mu_B H_o/kT \approx 3 \) shows that the Dy³⁺ spins are almost ferromagnetically aligned along the b direction in the fields above \( H_o \). This is confirmed by the magnetization measurement [10] at 4.2 °K and 1.7 °K. Then, the antisymmetric exchange interaction between Cr³⁺ (mainly Gₓ-type) and Dy³⁺ spins may induce the shifts saturating at \( H_o \).

In DyCrO₃ a weak electric-dipole band is observed at the low-energy side of the exciton lines as seen in figure 3 (\( H//b, E//a \)). The band shape is asymmetric with a relatively steep edge at the low-energy side. The band is most conspicuous for the polarization \( E//a \) (\( E \): the oscillating electric vector of the incident light). Its intensity, comparable to that of the exciton lines, shows noticeable decrease only when a magnetic field is applied along the b-axis. This band seems to
have the same origin as that already reported [6] in ErCrO$_3$. These qualitative features are explained by assuming that the band is due to the exciton transition accompanying a spin-flip of Dy$^{3+}$ ions. For this interpretation it is necessary to assume a negative dispersion ($\sim 16$ cm$^{-1}$) of the Cr$^{3+}$ exciton band.

References

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