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► **To cite this version:**

S. Sugano, Y. Uesaka, I. Tsujikawa, K. Aoyagi, K. Tsushima. EXCITON LINES IN RARE-EARTH ORTHOCHROMITES. *Journal de Physique Colloques*, 1971, 32 (C1), pp.C1-798-C1-800. 10.1051/jphyscol:19711281 . jpa-00214118

HAL Id: jpa-00214118

<https://hal.science/jpa-00214118>

Submitted on 4 Feb 2008

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EXCITON LINES IN RARE-EARTH ORTHOCHROMITES

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Résumé. — Nous avons étudié, dans des champs atteignant 50 kOe, parallèlement à l'axe a , les raies d'excitation provenant de l'ion Cr^{3+} raie-R de l'antiferromagnétique YCrO_3 de type G_x . La polarisation du spectre en champs forts est en accord avec la règle de sélection des antiferromagnétiques de type G_z , indiquant une réorientation de G_x à G_z des spins induite par le champ. Nous discutons d'autres preuves de la réorientation des spins. Dans DyCrO_3 (type G_z) quatre raies d'excitation apparaissent clairement lorsque le champ magnétique est appliqué le long de l'axe b . Nous discutons les propriétés particulières de ces raies d'excitation en supposant une interaction antisymétrique $\text{Cr}^{3+}\text{-Dy}^{3+}$.

Abstract. — The exciton lines arising from the Cr^{3+} R-line of the G_x -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_z -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_z -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 $\text{Cr}^{3+}\text{-Dy}^{3+}$ interaction.

Recently optical spectra of antiferromagnetic rare earth orthochromites are being studied by several research groups. In particular, the exciton lines associated with the $t_2^3 \ ^4A_2 \rightarrow t_2^3 \ ^2E$ 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 $\text{Cr}^{3+}\text{-Dy}^{3+}$ interaction.

The observed behavior of the exciton lines of YCrO_3 in magnetic fields up to 50 kOe parallel to the a axis (G_x -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_z -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] ($H_c = 37$ kOe) and is observed by Jacobs, Burne and Levinson ($H_c = 40 \pm 1$ 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

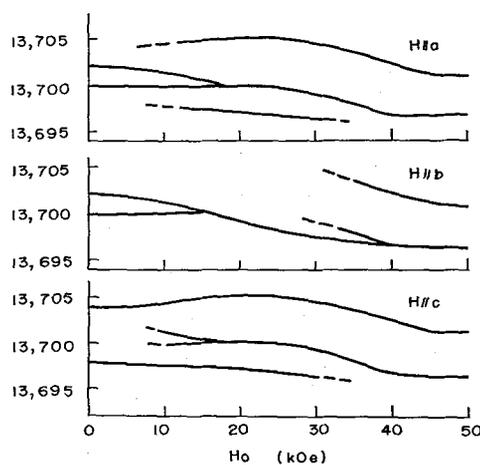


FIG. 1. — Exciton lines of YCrO_3 in magnetic fields $H_0//a$ at 4.2 °K. H is the magnetic vector of the incident light.

a -polarized line or the inapplicability of the selection rule for G_z . 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 CrO_6 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 ErCrO_3 , 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.

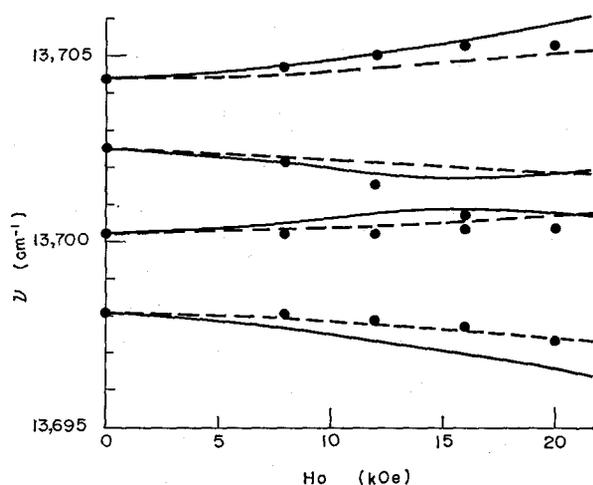


FIG. 2. — Frequency shifts of the exciton lines of YCrO_3 . The calculated shifts without spin reorientation: — for $g' = 1.0$, --- for $g' = 3.0$ (g' ; g -value of the single-ion excited state). The observed shifts: ●.

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 ν_{12} and ν_{14} , respectively, the matrix elements of the excitation transfer between the nearest-neighbour Cr^{3+} 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 ν_{12} is much smaller than ν_{14} ($\nu_{12} = 0.03 \text{ cm}^{-1}$, $|\nu_{14}| = 0.28 \text{ cm}^{-1}$), 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 G_x -type ErCrO_3 . This unexpected situation can be explained by considering the A_y -type [7] spin arrangement compatible with G_x : the A_y 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,

$$\nu_{12}(H_0) = \nu_{12}(0) + \alpha H_0^2 (\alpha > 0).$$

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

In DyCrO_3 , roughly speaking, two exciton lines are observed in the frequency range, $13\,680 \sim 13\,690 \text{ cm}^{-1}$, as in YCrO_3 . 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 G_z -type spin arrangement, if two Davydov components with the a - and b, c -polarizations are assumed to be nearly degenerate. This means that ν_{12} and ν_{14} are very small. By using the same argument as given for YCrO_3 , this may be ascribed to the absence (or smallness) of the C_y -type [7] component compatible with G_z .

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

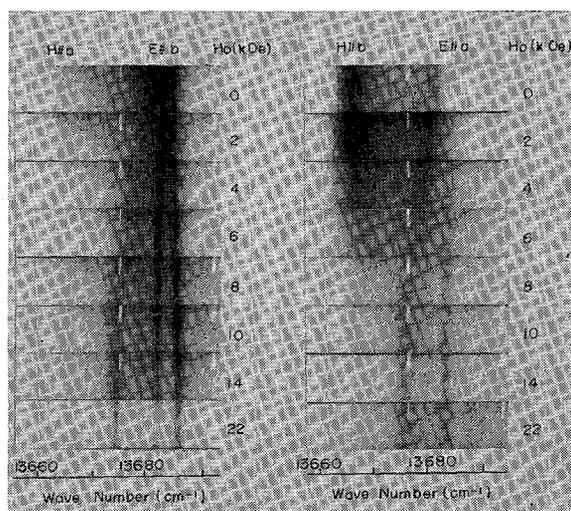


FIG. 3. — Exciton lines and the associated weak band of DyCrO_3 with $H_0//b$ at $4.2 \text{ }^\circ\text{K}$.

the magnetic field, H_s , which is dependent on temperature. The observed value of H_s at $1.7 \text{ }^\circ\text{K}$ is 4 kOe and it is 10 kOe at $4.2 \text{ }^\circ\text{K}$, which shows that $\mu_B H_s/kT$ is constant independent of temperature (μ_B : Bohr magneton).

Bearing in mind the fact deduced from the Dy^{3+} spectrum in DyCrO_3 that the g -value of the ground Kramers doublet of the Dy^{3+} ions is highly anisotropic ($g_b \approx 17$, $g_a < 3$, $g_c < 1$), we speculate that some Dy^{3+} - Cr^{3+} interaction is responsible for the observed shifts. In fact the value of $g_b \mu_B H_s/kT \approx 3$ shows that the Dy^{3+} spins are almost ferromagnetically aligned along the b direction in the fields above H_s . This is confirmed by the magnetization measurement [10] at $4.2 \text{ }^\circ\text{K}$ and $1.7 \text{ }^\circ\text{K}$. Then, the antisymmetric exchange interaction between Cr^{3+} (mainly G_z -type) and Dy^{3+} spins may induce the shifts saturating at H_s .

In DyCrO_3 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 ($\sim 16 \text{ cm}^{-1}$) of the Cr^{3+} exciton band.

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