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Crystal and magnetic structures of Y₂CrS₄

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Abstract

Chromium(II) sulfide, Y₂CrS₄, prepared by a solid-state reaction of Y₂S₃ and CrS, showed an antiferromagnetic transition at 65 K. The neutron diffraction patterns at 10 and 90 K were both well refined with the space group *Pca*2₁. At 90 K, cell parameters were a = 12.5518(13) Å, b = 7.5245(8) Å, and c = 12.4918(13) Å. At 10 K, magnetic peaks were observed, which could be indexed on the same unit cell. Magnetic moments of chromium ions were parallel to the *b*-axis and antiferromagnetically ordered in each set of the 4*a* sites. \bigcirc 2007 Elsevier Ltd. All rights reserved.

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1. Introduction

Divalent chromium ions are Jahn-Teller ions with d^4 configuration. They make complex sulfides with other cations but these sulfides have not been well studied. One of the examples is Er₂CrS₄, having an orthorhombic structure belonging to the space group $Pca2_1$ (No. 29) [1,2]. The results of the structure refinement suggested that CrS₆ octahedra in this structure were distorted by the Jahn-Teller effect. Other rare-earth elements were also reported to form R_2CrS_4 (R = Y, Ho–Tm) that crystallized in the same structure [3,4], though their detailed crystal structures were not investigated. Electronic properties have not been studied for any of these compounds. Since the yttrium ion is diamagnetic, Y2CrS4 is suitable for the investigation of magnetic behavior of chromium ions in Er₂CrS₄-type compounds. In this study, we investigated the crystallographic and magnetic properties of Y₂CrS₄.

2. Experimental

 Y_2CrS_4 was prepared by a solid-state reaction. Yttrium sulfide (Y_2S_3) and chromium sulfide (CrS) were used as starting materials. In order to obtain yttrium sulfide, yttrium oxide (Y_2O_3) was heated in a silica boat at 1000 °C in a flow of the mixed gas of CS_2 and N_2 which was obtained by bubbling the N_2 gas through liquid CS_2 at room temperature. Chromium sulfide was synthesized by heating the mixture of chromium and sulfur at 1000 °C in an evacuated silica tube. The starting materials were stoichiometrically mixed together and sealed in an evacuated silica tube. The tube was heated at 1300 °C for 24 h.

Powder X-ray diffraction (XRD) patterns were measured with Cu K α radiation on a RINT2000 diffractometer (Rigaku) equipped with a graphite monochromator.

The magnetic susceptibilities were measured under an applied field of 0.1 T in the temperature range between 4.5 and 300 K by using a SQUID magnetometer (Quantum Design, MPMS-5S).

Powder neutron diffraction measurements were carried out using the Kinken powder diffractometer for highefficiency and high-resolution measurements, HERMES, of Institute for Material Research, Tohoku University, installed at the JRR-3M reactor in Japan Atomic Energy Agency (JAEA), Tokai. Neutrons with wavelength of 1.81430 Å were obtained by the 331 reflection of the Ge monochromator and 120-blank-220 collimation [5]. The sample was set in a 10 mm diameter vanadium cylinder, which was sealed in a standard aluminum cell under a helium gas and cooled with a liquid helium cryostat. Intensity data from 3° to 145° were used in the crystal structure and magnetic structure refinements using Rietveld method program RIETAN [6].

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3. Results and discussion

3.1. Crystal structure

 Y_2CrS_4 prepared in this study is formed in a single phase. The powder X-ray diffraction pattern was successfully analyzed with an orthorhombic unit cell, space group $Pca2_1$ (No. 29) by the Rietveld method, the structure of

Table 1 Crystallographic data for Y_2CrS_4 at room temperature

Space group			<i>Pca</i> 2 ₁ (No. 29)	
a (Å) b (Å) c (Å) R _{wp} (%) s	12.5686(3) 7.5548(2) 12.4942(3) 7.67 1.71			
Atoms	X	У	Ζ	
Crl	0.3798(7)	0.888(2)	0.1863(7)	
Cr2	0.3966(6)	0.387(2)	0.8131(9)	
Y1	0.3802(5)	0.8912(9)	0.813	
Y2	0.6335(5)	0.8638(9)	0.0115(4)	
Y3	0.3815(5)	0.3793(9)	0.1699(4)	
Y4	0.6391(4)	0.3650(8)	0.9921(5)	
S 1	0.5386(11)	0.598(2)	0.1222 (11)	
S2	0.5201(12)	0.602(2)	0.8624(14)	
S 3	0.2863(10)	0.880(3)	0.0035(11)	
S4	0.7693(8)	0.8879(15)	0.7311(10)	
S 5	0.5111(12)	0.114(2)	0.1253(15)	
S 6	0.5427(11)	0.137(2)	0.8641(12)	
S 7	0.2964(9)	0.371(3)	0.9759(11)	
S 8	0.7433(10)	0.364(2)	0.7326(9)	

Note: All atoms were in 4a sites. All isotropic atomic displacement parameters (*B*) were fixed to be 0.3 Å².





Fig. 2. Crystal structure of Y2CrS4.



Fig. 1. Powder X-ray diffraction pattern fitting for Y_2CrS_4 . The calculated and observed patterns are shown on the top solid line and the cross markers, respectively. The vertical marks in the middle show positions calculated for Bragg reflections. The lower trace is a plot of the difference between calculated and observed intensities.



Fig. 3. Distortions of CrS₆ octahera.

Table 2 Cell parameters for Y_2CrS_4

T (K)	a (Å)	<i>b</i> (Å)	<i>c</i> (Å)
RT	12.5686(3)	7.5548(2)	12.4942(3)
90	12.5518(13)	7.5245(8)	12.4918(13)
10	12.543(2)	7.5223(9)	12.492(2)

Jahn–Teller effect of divalent chromium ions, similar to those in Er_2CrS_4 .

The neutron diffraction patterns at 10 and 90 K were both well refined with the space group $Pca2_1$ (No. 29) by using atomic positions in Table 1. At 90 K, lattice parameters were determined to be a = 12.5518(13) Å, b = 7.5245(8) Å, and c = 12.4918(13) Å. At 10 K, lattice parameters were determined to be a = 12.543(2) Å, b = 7.5223(9) Å, and c = 12.492(2) Å. The lattice parameters are listed in Table 2. The lattice parameters in this sulfide increased with increasing temperatures.

3.2. Magnetic property

Magnetic susceptibilities were measured in the temperature range between 4.5 and 300 K. Fig. 4 shows temperature dependence of magnetic susceptibilities for Y_2CrS_4 . Antiferromagnetic anomaly was observed at 65 K. The susceptibility obeyed the Curie–Weiss law above 200 K. The effective magnetic moment was experimentally determined to be 4.69(1) μ_B from the Curie–Weiss fitting. The theoretical effective magnetic moments of Cr^{2+} in the highspin state and in the low spin state, are 4.90 and 2.83 μ_B ,



Fig. 4. Magnetic susceptibility vs. temperature for Y_2CrS_4 . The inset shows the inverse magnetic susceptibilities as a function of temperature.

respectively. The effective magnetic moments indicated that chromium ions had $3d^4$ high-spin state. The Weiss constant was determined to be a positive value, 28.2(8) K though antiferromagnetic behavior was observed. Differences between ZFC and FC were observed below Néel temperature. These results suggest that the magnetic moments of Cr in Y₂CrS₄ order with a slight ferromagnetic component below Néel temperatures.



Fig. 5. Powder neutron diffraction patterns of Y_2CrS_4 at (a) 10 K and (b) 90 K. Indices for magnetic reflections are based on crystallographic unit cell.



Fig. 6. Magnetic structure of Y₂CrS₄ at 10K.

3.3. Magnetic structure

In order to determine the changes in its magnetic structures at the magnetic transition, neutron diffraction measurements were performed above and below T_N , 90 and 10 K. At 10 K, several additional Bragg peaks were observed indicating magnetic ordering as shown in Fig. 5. These magnetic peaks could be indexed on the same crystallographic unit cell. Thus, superlattice or satellite peak was not observed. This indicates that the magnetic propagation vector is a null vector [0, 0, 0]. Under this condition, the possible magnetic structure of the 4*a* site of space group was estimated by the representation analysis technique (program SARAh [7]).

The structure contains two kinds of chromium sites, Cr1 and Cr2, both of them occupying the 4a Wyckoff positions of the orthorhombic space group $Pca2_1$. We first discuss the magnetic arrangement of Cr1 ions. Their positions are:

Position	X	У	Ζ
Crl_1	0.3798(6)	0.888(2)	0.1863(7)
Crl_2	0.6202(6)	0.112(2)	0.6863(7)
$Cr1_3$	0.8798(6)	0.112(2)	0.1863(7)
Cr1 ₄	0.1202(6)	0.888(2)	0.6863(7)

The Cr1 ions have respective magnetic moments S_1 , S_2 , S_3 , and S_4 , and four types of magnetic arrangements are possible:

$$F = S_1 + S_2 + S_3 + S_4$$

$$A1 = S_1 + S_2 - S_3 - S_4$$

$$A2 = S_1 - S_2 + S_3 - S_4$$

$$A3 = S_1 - S_2 - S_3 + S_4$$



Fig. 7. Powder neutron diffraction pattern fittings for Y_2CrS_4 at 10 K. The calculated and observed patterns are shown on the top solid line and the cross markers, respectively. The first vertical marks in the middle show positions calculated for nuclear Bragg reflections. The second vertical marks show positions calculated for magnetic reflections. The lower trace is a plot of the difference between calculated and observed intensities.

The calculation of the representation analysis showed that different sets of magnetic modes were possible, i.e., for the irreducible representation Γ_1 with the A2_x, A3_y, and A1_z modes; Γ_2 with the A3_x, A1_y, and F_z modes; Γ_3 with the F_x , $A1_y$, and $A3_z$ modes; and Γ_4 with the $A1_x$, F_y , and $A2_z$ modes (the subscripts show the direction of magnetic moments). Cr2 ions also could be discussed in the same way and the combinations of the magnetic arrangements of Cr1 and Cr2 ions gave a large number of possibilities. Then, we assumed that the ordered magnetic moments of chromium ions at the two sets of 4a sites had the same magnitude and adopted a collinear arrangement. This assumption led to a successful Rietveld refinement giving the magnetic structure shown in Fig. 6. The result of powder neutron pattern fitting by using this magnetic structure is shown in Fig. 7. In this structure, magnetic moments of chromium ions order antiferromagnetically in each set of the 4a sites. The directions of all magnetic moments are parallel to the *b*-axis, i.e, the $A1_v$ mode dominates for Y_2CrS_4 at 10K. The mode belongs to the irreducible representation Γ_3 . The magnetic susceptibility of the compound indicates that it has a weak ferromagnetic moment of chromium (F-type) at 10K. However, the reflection intensities due to the ferromagnetic diffractions are too weak compared with those due to the nuclear diffraction, and the component of the magnetic moment with F-type could not be estimated. It seems most probable that the ferromagnetic component is parallel to the x-axis because the F_x mode transforms according to the irreducible representation Γ_3 , to which the arrangement of the antiferromagnetic moments belongs. The refined magnetic moment of Cr^{2+} is $3.27(9) \mu_B$, which is slightly smaller than $4\mu_B$ expected from the $3d^4$ electronic configuration.

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