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Preparation and Physical Properties of Fe_xTaS_2 ($0.15 \leq x \leq 0.50$) Compounds

H. Narita, H. Ikuta, H. Hinode, T. Uchida, T. Ohtani,* and M. Wakihara[1]

*Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152 Japan; and *Laboratory for Solid State Chemistry, Okayama University of Science, 1-1 Ridai-cho, Okayama 700, Japan*

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The intercalation compounds of the Fe–Ta–S system were synthesized by heating the mixture of 1T–TaS_2 and metal Fe in a sealed evacuated silica tube. The single phase region was $0.15 \leq x \leq 0.50$ in Fe_xTaS_2. The hexagonal a-axis was almost constant, while the c-axis increased simply with increasing iron content x. Temperature dependence of electrical resistivity showed metallic behavior. Mössbauer effect measurements showed that the iron was high-spin state Fe^{2+} in Fe_xTaS_2. The temperature variation of magnetic susceptibility obeyed a Curie–Weiss law. The Weiss temperature θ decreased with x and changed the value from positive to negative at $x \simeq 0.4$ suggesting the change of exchange interactions from ferromagnetic to antiferromagnetic.

1. INTRODUCTION

The disulfides of tantalum have a layered structure consisting of S–Ta–S sandwiches with a weak interaction between them. The van der Waals gap between the sandwiches can be intercalated with large atoms or molecules. In the van der Waals gap intercalated transition metal is coordinated tetrahedrally or octahedrally by sulfur atoms. Usually the gap is called the partially occupied layer. In Fe_xTaS_2 many studies have been made extensively in terms of crystal structure (1, 2), electrical properties (3, 4), magnetic properties (1–5), band structure calculations (6) and Mössbauer spectroscopy (3, 7). However, they were limited to compounds with special iron content such as $Fe_{1/4}TaS_2$, $Fe_{1/3}TaS_2$, and $Fe_{1/2}TaS_2$.

Here we have synthesized Fe_xTaS_2 with various compositions and have determined the single phase region of Fe_xTaS_2 using powder X-ray diffraction method. Then, the physical properties such as electrical resistivity, Mössbauer effect, and magnetic susceptibility of these compounds have been studied.

2. EXPERIMENTAL

Synthesis

Small tips cut from Ta foil (Sanwa Metal Co., 99.9%) and excess elemental sulfur (Wako Pure Chemical Industries, Ltd., 99.9999%) were loaded in a silica tube under vacuum. The tube was heated at 1000°C for 3 weeks, and unreacted Ta metals were removed from the product. The compounds TaS_x ($x < 2$) with sulfur were heated in an evacuated silica tube at 1000°C for 2 weeks to form stoichiometric 1T–TaS_2. Ternary Fe_x–TaS_2 was prepared by mixing the prepared 1T–TaS_2 and metallic iron (Soekawa Chemical Co. Ltd., 99.9%, −100 mesh) with a desired ratio, pressing the mixture into a pellet, and heating the pellet in an evacuated silica tube. These were first annealed at 400°C for 12 hr and finally at 1000°C for 2 weeks, followed by quickly cooling to room temperature. The phase identification of the products was carried out by powder X-ray diffractometry using Cu$K\alpha$ radiation obtained from a high-power X-ray generator (Rotaflex RU-200A, Rigaku Co. Ltd.).

Physical Measurements

The electrical resistivity measurement on the samples (diameter 4 mm × thickness 8 mm) was performed using the DC four-probe technique in the temperature range 90–300 K. All measurements were made in H_2 atmosphere. For Fe_xTaS_2 in the range $x < 0.20$, the measurement could not be carried out because of the difficulty of sintering.

The magnetic susceptibilities were measured in the temperature range 80–300 K using a Faraday method. For $Fe_{0.22}TaS_2$ and $Fe_{0.25}TaS_2$, the measurements were performed only at $T > 150$ K because of the appearance of ferromagnetism at $T \simeq 150$ K.

For the ^{57}Fe Mössbauer experiment, the source was ^{57}Co in an Rh matrix. The center shift was referred to

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[1] To whom correspondence should be addressed.

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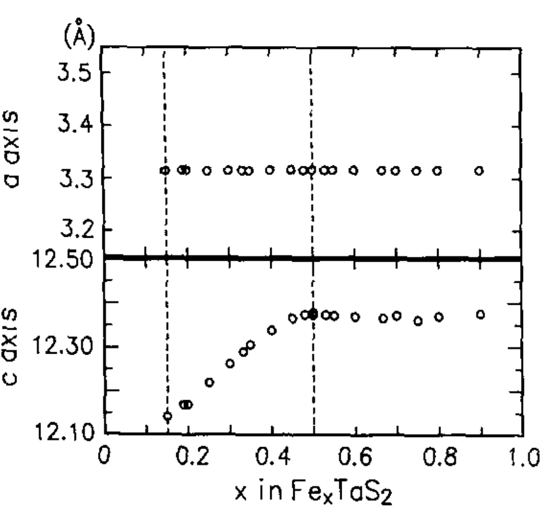

FIG. 1. Plots of lattice parameters of Fe_xTaS_2.

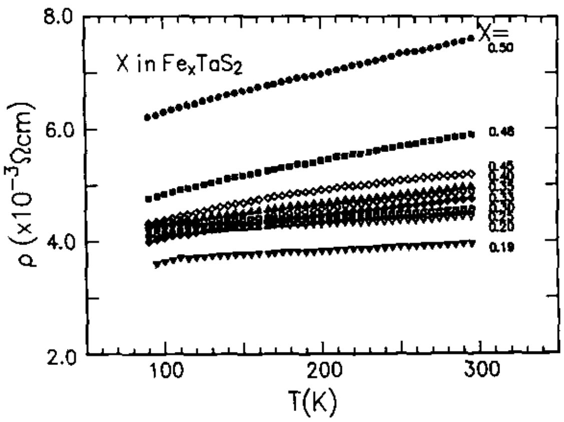

FIG. 2. Electrical resistivity of Fe_xTaS_2.

pure metal iron. The measurements were performed at 295 K using powdered samples suspended on paper with a cellulose adhesive. An exposure time of a few days was required to obtain a reliable absorption spectrum, depending on the iron content of the samples.

3. RESULTS AND DISCUSSION

All the powder X-ray diffraction patterns of the compounds Fe_xTaS_2 in the range $0.15 \leq x \leq 0.50$ were indexed on a hexagonal unit cell similar to 2Ha–TaS_2. Accordingly the single phase region was $0.15 \leq x \leq 0.50$. Mixed phases of 1T-type and 2Ha-type were observed in the powder X-ray diffraction patterns of the compounds Fe_xTaS_2 in the range $x < 0.15$. Ferromagnetism from unreacted Fe was recognized in the compounds Fe_xTaS_2 in the range $x > 0.50$. Relations between the iron content x and the hexagonal lattice parameters a and c are shown in Fig. 1. For $Fe_{1/3}TaS_2$ they are 3.315 and 12.290 Å, respectively, almost consistent with the literature values (2). In the single phase region, the lattice parameter a was almost unchanged while the lattice parameter c increased almost linearly with an increase of the iron content x (Fig. 1). This means that the iron ions inserted into the partially occupied layers expand the van der Waals gaps.

The electrical resistivity data in the temperature range 90–300 K are presented in Fig. 2. The resistivity increased with increasing temperature in all the samples, which indicated metallic behavior similar to that of 2Ha–TaS_2 (4). The room temperature resistivity (Fig. 3) of our samples was larger than the value, $\rho = 2.7 \times 10^{-4}$ Ω cm, of single crystal $Fe_{0.28}TaS_2$ parallel to the layer reported by Eibschütz *et al.* (3). Because in general, the resistivity perpendicular to the layer is larger than that of parallel one in the layer compounds. Accordingly the value of resistivity in our powder samples fell in the middle of $\rho_\perp$ and $\rho_\parallel$. The resistivity at room temperature was almost constant in the range $x < 0.40$, and remarkably increased in $x \geq 0.45$.

Assuming the rigid band model that the band structure of the host molecular TaS_2 has no change with Fe intercalation (8), the d_{z^2} band of TaS_2 can accommodate one electron because the Fermi level in the host TaS_2 lies in the middle of the d_{z^2} band. The resistivity at room temperature reached largest value at $x = 0.50$ (Fig. 3). Therefore the $Fe_{0.50}$ donates one electron to the host molecular TaS_2 and the d_{z^2} band is entirely filled suggesting that the valence of iron is divalent.

Moreover, according to a well-known empirical rule on the relationship between the coordination number and the ratio of cation radius to anion radius (9), the valence of iron could be speculated. The rule states that octahedral coordination is most stable if $0.414 \leq r_{cat}/r_{ani} < 0.527$, where r_{cat} and r_{ani} are the radius of cation and anion, respectively. The octahedral Fe atoms are coordinated by S atoms in Fe_xTaS_2. Assuming $a/2 = 1.66$ Å for S^{2-}

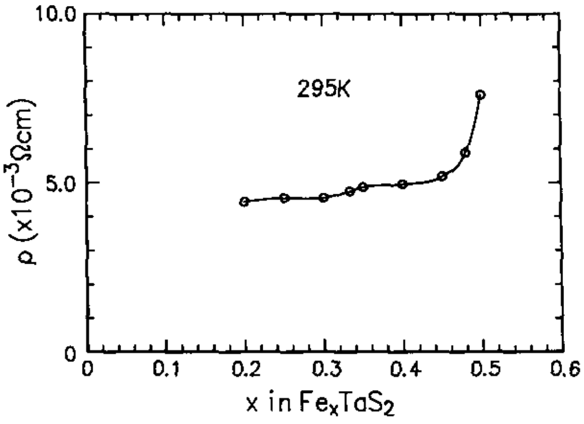

FIG. 3. Room temperature resistivity of Fe_xTaS_2.

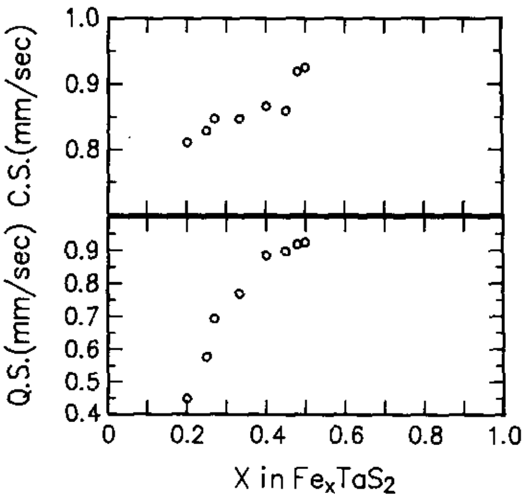

FIG. 4. Plots of center shift (CS) and quadrupole splitting (QS) of Fe_xTaS_2.

as r_{ani} for TaS_2, r_{cat} falls in $0.69 \leq r_{cat} < 0.87$ Å. This suggests that the ionic state of iron is divalent because the radius of Fe^{2+} and Fe^{3+} is 0.76 and 0.64 Å, respectively (10).

The Mössbauer absorption spectra of Fe_xTaS_2 showed two resonance lines due to the electric field gradient at the iron nucleus. At room temperature the center shift (CS) is in the range of 0.83–0.92 mm/sec (Fig. 4) showing that the iron atoms are in the high-spin Fe^{2+} state. The values of the CS increased with increasing the iron content x, which indicates that the electronic density around the iron nuclei decreases with x. The values of quadrupole splitting increase with increasing the iron content x, suggesting that the electric field gradient in the iron nuclei increases by distortion of FeS_6 octahedra. The distortion was attributed to the increase of the c parameter by intercalation of the iron in the van der Waals gap.

In all the samples the temperature dependence of magnetic susceptibility obeyed a Curie–Weiss law (Fig. 5) described by

$$\chi = \chi_0 + \frac{C_{mol}}{T - \theta},$$

where χ_0 is a temperature-independent term, C_{mol} is a molar Curie constant, and θ is a Weiss constant. The results are shown in Fig. 5. The values of C_{mol} and θ in Table 1 were obtained by using a least squares analysis. θ decreased with increasing the iron content x and was negative at $x = 0.45$, suggesting the magnetic interactions changed from ferromagnetic to antiferromagnetic at $x \simeq 0.4$. It may originate from shorter Fe–Fe distance with an increase of the iron content x (11).

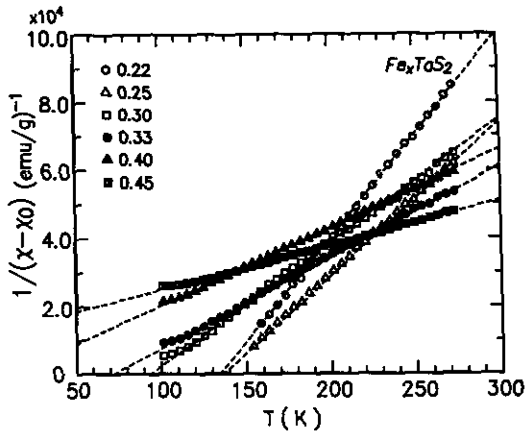

FIG. 5. Curie–Weiss behavior of Fe_xTaS_2.

P_{eff} is an effective Bohr magneton per an Fe atom calculated by using the values of C_{mol}, and values of S obtained by assuming that only spins contribute to C_{mol} showed that the valence of iron is expected to be predominantly +2 except for $x = 0.45$. These results are compatible with those of electrical resistivity and Mössbauer spectroscopy measurements. An enormously large value of P_{eff} of the sample at $x = 0.45$ would be owing to the effect of non-quenching of orbital angular momentum. Similar behavior has been observed in $Fe_{1/3}TaS_2$ single crystal (5).

4. CONCLUSIONS

The results are summarized as follows:

(1) The iron content in single phase of Fe_xTaS_2 is $0.15 \leq x \leq 0.50$. The hexagonal lattice parameter a is almost constant, but c increases with an increase of the iron content x.

(2) In the electrical resistivity measurements, metallic behavior is observed in all the samples, and the resistivity in room temperature remarkably increases in the range $x \geq 0.45$.

(3) The values of center shift in Mössbauer effect measurements suggest that the valence of Fe is divalent +2 ($S = 2$) in Fe_xTaS_2.

TABLE 1
Magnetic Parameters of Fe_xTaS_2

	χ_0 ($\times 10^{-6}$ emu/g)	C_{mol}	θ (K)	P_{eff} (μ_B)
$Fe_{0.25}TaS_2$	−3.00	2.26	135.5	4.27
$Fe_{0.30}TaS_2$	−2.68	2.44	91.3	4.44
$Fe_{0.33}TaS_2$	−4.94	2.97	70.4	4.89
$Fe_{0.40}TaS_2$	−3.35	2.95	10.3	4.88
$Fe_{0.45}TaS_2$	4.16	4.50	−85.0	6.03

(4) The magnetic susceptibility obeys a Curie–Weiss law in all the samples.

The magnetic interactions change from ferromagnetic to antiferromagnetic near $x = 0.4$, accompanying with the change of Fe–Fe distance.

The values of C_{mol} show that the state of iron ions is nearly equal to +2.

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