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Magnetic Susceptibility and Torque Measurements of FeV_2S_4, FeV_2Se_4 and $FeTi_2Se_4$

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Magnetic susceptibility and torque measurements of FeV_2S_4, FeV_2Se_4 and $FeTi_2Se_4$ were made using the powder and the single crystal samples. The inverse susceptibility of FeV_2S_4, FeV_2Se_4 and $FeTi_2Se_4$ changed its slope at 850, 820 and 700 K, respectively, at which temperature the order–disorder transition of cation vacancies should seem to take place. Above these temperatures the paramagnetic moment obtained for these compounds was in the range of 5.26–5.37 μ_B, close to that of the high spin state Fe^{2+}. Below these temperatures the paramagnetic moment was reduced to 4.23–4.35 μ_B.

The antiferromagnetic spin axis of FeV_2S_4 was in the neighborhood of the [101] direction and that of FeV_2Se_4 and $FeTi_2Se_4$ in the direction of the *c*-axis. The large magnetic anisotropy observed and the preference of the magnetic moments for the direction of the *c*-axis were attributed to the spin-orbit interaction of Fe^{2+} electrons in the trigonal crystal field.

Introduction

The crystal structure of FeV_2S_4 (*1*), FeV_2Se_4 (*2*) and $FeTi_2Se_4$ (*3*) is isomorphous with Cr_3S_4, in which cation vacancies are confined to the alternate metal layers as shown in Fig. 1. Iron atoms occupy the vacant layers, while titanium or vanadium atoms occupy the metal filled layers. Magnetic susceptibility of FeV_2S_4, FeV_2Se_4 and $FeTi_2Se_4$ was measured from 77 to 300 K by Morris et al. (*4*). They were antiferromagnet with the Néel point at 131 K for FeV_2S_4, 94.5 K for FeV_2Se_4 and 134 K for $FeTi_2Se_4$, respectively. The paramagnetic moment of iron atoms in these compounds was 4.15–4.18 μ_B, provided that the Ti or V electrons were completely delocalized. Though the values obtained were rather small compared with the spin only value of Fe^{2+}, 4.91 μ_B, they considered that the electronic state of iron atoms was high spin state Fe^{2+} and that the partial delocalization of Fe^{2+} electrons was responsible for the reduced paramagnetic moments.

The isomorphous compound $FeTi_2S_4$ was also antiferromagnet with the Néel point at 138 K, though its magnetic properties were greatly affected by the heat treatments during the sample preparation (*5*, *6*). The paramagnetic moment below room temperatures obtained from the single crystal samples was 3.95 μ_B, and 3.45 μ_B for the parallel and the perpendicular susceptibility to the spin axis in the *c*-axis direction, respectively (*7*). However, above 720 K, at which temperature the order–disorder transition of cation vacancies has taken place, the paramagnetic moment was 5.26 μ_B (*6*), close to that of Fe^{2+}. The iron ions in $FeTi_2S_4$ have been, therefore, considered to be in a high spin state Fe^{2+}. Similar behaviors of the paramagnetic moment are expected for FeV_2S_4, FeV_2Se_4 and $FeTi_2Se_4$ above room temperatures.

The magnetic susceptibility of these three compounds was measured from 4 to 1240 K using the powder samples prepared under the careful heat treatments. In addition to these measurements, the magnetic susceptibility and torque measurements were carried out using the single crystal samples in order to

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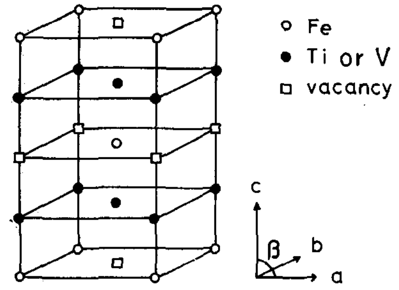

FIG. 1. Metal ion arrangement in FeV_2S_4, FeV_2Se_4 and $FeTi_2Se_4$. Hexagonal array of sulfur or selenium is omitted.

study further the magnetic properties of these compounds.

Experimental Procedures

Powder samples of FeV_2S_4, FeV_2Se_4 and $FeTi_2Se_4$ were prepared by a direct reaction of highly pure elements in an evacuated silica tube. After heated at 500°C, the mixture was ground and again heated at 900°C for one week. The sample was then slowly cooled to room temperature.

Chemical and X-ray analyses ensured that the prepared samples were stoichiometric, monoclinic compounds. Monoclinic lattice parameters of FeV_2S_4 were $a = 5.87$, $b = 3.30$, $c = 11.30$ Å and $\beta = 92.00°$. Those of FeV_2Se_4 were $a = 6.19$, $b = 3.47$, $c = 11.79$ Å and $\beta = 91.60°$. Those of $FeTi_2Se_4$ were $a = 6.23$, $b = 3.59$, $c = 11.96$ Å and $\beta = 90.20°$. The lattice parameters obtained for these three compounds were in agreement with the results of (*1*, *2*) and (*3*) within the accuracy of $\pm 0.5\%$.

Single crystals of FeV_2S_4, FeV_2Se_4 and $FeTi_2Se_4$ were grown by the isothermal vapor growth in the closed silica tube, using Cl_2 or $TeCl_4$ as a growth agency. The detailed procedures of the crystal growth experiments have been already reported by the authors (*8*). The crystals obtained by this method were examined by the chemical and X-ray precession methods. The crystals of FeV_2S_4 and $FeTi_2Se_4$ were confirmed to be stoichiometric single crystals, whereas the stoichiometric crystals of FeV_2Se_4 partially twinned in the *c* plane. The crystals used for the magnetic susceptibility measurements had the weight of about 20 mg for FeV_2S_4, 8 mg for FeV_2Se_4 and 12 mg for $FeTi_2Se_4$, respectively.

Results and Discussion

1. *Susceptibility of the Powder Samples*

Magnetic susceptibility of FeV_2S_4, FeV_2Se_4 and $FeTi_2Se_4$ was measured from 4 to 1240 K with the torsion balance magnetometer. In order to avoid the oxidation the measurements above room temperatures were made using the samples evacuated in silica tube.

The sample of FeV_2S_4, FeV_2Se_4 and $FeTi_2Se_4$ was antiferromagnet with the Néel point at 140, 107 and 134 K, respectively, slightly higher than the values reported Morris et al. (*4*). The difference of the Néel points should be attributed to the heat treatments during the sample preparation besides the slight difference of the chemical compositions, since the samples quenched from 900°C had the Néel point at 114 K for FeV_2S_4, 89 K for FeV_2Se_4 and 129 K for $FeTi_2Se_4$, respectively. It is supposed that the order degree of cation vacancies affected somewhat the magnetic properties for these compounds.

The susceptibility of FeV_2S_4, FeV_2Se_4 and $FeTi_2Se_4$ was corrected for the temperature independent susceptibility. In addition to the negative contribution from the core diamagnetism, there should be a positive Pauli paramagnetic contribution from conduction electrons, because these compounds exhibited metallic behaviors with the resistivity of 10^{-3}–10^{-4} Ω cm at room temperature (*8*, *9*). It is, however, difficult to estimate accurately the temperature independent susceptibility of these compounds. The susceptibility of FeV_2S_4 above 850 K, FeV_2Se_4 above 820 K and $FeTi_2Se_4$ above 700 K was made fit with the equation $\chi = \chi_c + C/T + \theta$, where the former term, χ_c, is the temperature independent susceptibility and the latter the temperature dependent one which obeys the Curie–Weiss law. The value of the correction obtained for FeV_2S_4, FeV_2Se_4 and $FeTi_2Se_4$ was 2.8, 2.2 and 0.5 emu/g, respectively. The Pauli paramagnetic susceptibility of FeV_2S_4 and FeV_2Se_4, which is probably attributed to the completely delocalized electrons of V atoms, is considered to be greater than the core diamagnetism, while the paramagnetism and diamagnetism of $FeTi_2Se_4$ seem to almost cancel each other as in the case of $FeTi_2S_4$ for which no correction was made in the previous study (*6*).

The susceptibility of FeV_2S_4, FeV_2Se_4 and $FeTi_2Se_4$ above the Néel point was corrected using the temperature independent term obtained from the high temperatures. The inverse susceptibility of FeV_2S_4 and FeV_2Se_4 is shown in Fig. 2 and that of $FeTi_2Se_4$ in Fig. 3. For the comparison the susceptibility of $FeTi_2S_4$ is also shown in Fig. 4.

The inverse susceptibility of these compounds changed its slope from the Néel point to 1240 K and was divided into the three temperature ranges. When the Curie–Weiss law was applied for the respective temperature ranges, the paramagnetic moments and the paramagnetic Curie temperatures were obtained. Table I shows the Curie–Weiss parameters for FeV_2S_4, FeV_2Se_4 and $FeTi_2Se_4$, together with those of $FeTi_2S_4$ for which the values below 720 K were not derived in the previous study (*6*).

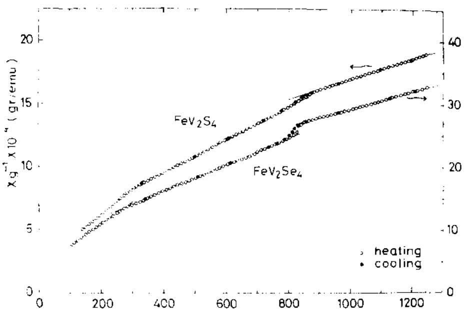

FIG. 2. Inverse magnetic susceptibility of FeV_2S_4 and FeV_2Se_4, corrected for the temperature independent paramagnetism.

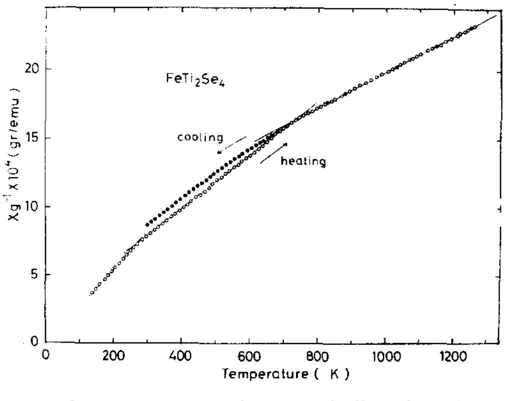

FIG. 3. Inverse magnetic susceptibility of $FeTi_2Se_4$, corrected for the temperature independent paramagnetism.

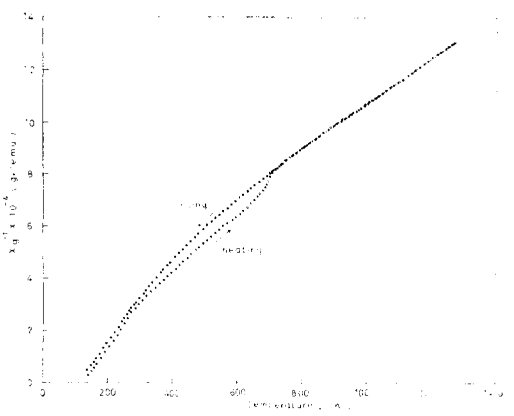

FIG. 4. Inverse magnetic susceptibility of $FeTi_2S_4$ from (*6*).

The paramagnetic moment of FeV_2S_4 above 850 K, FeV_2Se_4 above 820 K and $FeTi_2Se_4$ above 700 K was 5.32, 5.26 and 5.37 μ_B, respectively. This indicates that the iron ions in these compounds are high spin state Fe^{2+}

TABLE I

PARAMAGNETIC MOMENTS AND PARAMAGNETIC CURIE TEMPERATURES OF FeV_2S_4, FeV_2Se_4 AND $FeTi_2Se_4$ IN THE THREE TEMPERATURE RANGES, TOGETHER WITH THOSE OF $FeTi_2S_4$

	T(K)	P_{eff} (μ_B)	θ_p (K)
FeV_2S_4	140 ~ 300	3.40	−115
	300 ~ 850	4.23	−350
	850 ~ 1240	5.32	−1100
FeV_2Se_4	110 ~ 270	3.33	−122
	270 ~ 820	4.26	−370
	820 ~ 1240	5.26	−1125
$FeTi_2Se_4$	140 ~ 270	3.61	+10
	270 ~ 700	4.35	−148
	700 ~ 1240	5.37	−500
$FeTi_2S_4$	140 ~ 280	3.51	+125
	280 ~ 720	4.56	+15
	720 ~ 1270	5.26	−315

as in the case of $FeTi_2S_4$. Below these temperatures the paramagnetic moment was rather small value, 4.23 μ_B for FeV_2S_4, 4.26 μ_B for FeV_2Se_4, 4.35 μ_B for $FeTi_2Se_4$ and 4.56 μ_B for $FeTi_2S_4$, compared with the spin only value of Fe^{2+}, 4.91 μ_B. The paramagnetic moment below about room temperatures was further reduced to 3.40 μ_B for FeV_2S_4, 3.33 μ_B for FeV_2Se_4, 3.61 μ_B for $FeTi_2Se_4$ and 3.51 μ_B for $FeTi_2S_4$, respectively.

It was evidenced from the previous study for $FeTi_2S_4$ (*6*) that the kink of the susceptibility of $FeTi_2S_4$ at 720 K has been caused by the order–disorder transition of cation vacancies. The kink of FeV_2S_4, FeV_2Se_4 and $FeTi_2Se_4$ at high temperature is similarly considered to correspond to the change of the order degree of cation vacancies. The magnetic susceptibility of $FeTi_2Se_4$ below the kink point showed the different behavior in heating and cooling process as shown in Fig. 3. The susceptibility of FeV_2S_4 and FeV_2Se_4 had the small hysteresis at the kink point at 860 and 820 K, respectively, as shown in Fig. 2.

The reduction of the paramagnetic moment below these kink points is unexplainable at the present stage. However, as one of the possibilities it is supposed that the electrons of iron atoms in the vacancy ordered state are partially delocalized by forming the d band from the direct overlap of Fe^{2+} electrons as suggested by Morris et al. (*4*), and that in the disordered state of vacancies the partial disturbance of these overlapping causes the localized state of Fe^{2+} electrons.

2. *Magnetic Torque Measurements*

The magnetic torque measurements were carried out with the torque magnetometer in order to determine the antiferromagnetic spin axis of FeV_2S_4, FeV_2Se_4 and $FeTi_2Se_4$. The torques were measured at 4 and 80 K along the *a*-axis, *b*-axis and *c**-axis, respectively, where the *c**-axis is perpendicular to both of the *a*-axis and *b*-axis.

If the magnetic susceptibility of the principal axis for the antiferromagnetic or the paramagnetic compounds is χ_X, χ_Y and χ_Z, the torque curve rotated along the *Z*-axis can be expressed by the equation

$$T = 1/2(\chi_Y - \chi_X)\,H^2 \sin(2\theta + \varepsilon)$$

where θ is the angle of the direction of the magnetic field from the *X*-axis and ε is the phase angle, in the present case the angle between the *X*-axis and the *a*-axis, *b*-axis or *c**-axis.

The principal axes of the susceptibility tensor of FeV_2S_4, FeV_2Se_4 and $FeTi_2Se_4$ could be determined at 4 and 80 K. At both temperature one of the principal axis direction coincided with the *b*-axis, the other two lay in the *ac* plane for all three compounds. These results are consistent with the site symmetry arguments of iron lattice positions, C_{2h}.

The direction of the antiferromagnetic spin axis is regarded as the direction of the minimum susceptibility of the three principal susceptibilities below the Néel point. The magnitude differences of the principal susceptibilities could be also determined by the torque curves at 4 K.

(i) FeV_2S_4: The principal axis in the *ac* plane made the angle of 21° with the *c**-axis or the *a*-axis at both temperatures of 4 and 80 K. The direction of the spin axis, the direction of the minimum susceptibility, made the angle of 21° with the *c**-axis with the uncertainty ±3°, which arose from the misorientation of the crystals. This direction is in the neighborhood of the [101] direction which inclines the angle of 26° from the *c**-axis in the *ac* plane. The torque curves of FeV_2S_4 in the various magnetic fields at 4 K are shown in Fig. 5, together with the dependence of the torque amplitude on the square of the magnetic field. The torque amplitude changed linearly with the square of the magnetic field as expected from the torque equation. In this figure the *c**-axis is replaced by the *c*-axis, since they approximately coincide with each other within the experimental error of ±3°.

(ii) FeV_2Se_4 and $FeTi_2Se_4$: the principal axes of the susceptibility tensor of FeV_2Se_4 and $FeTi_2Se_4$ coincided with the *a*-axis, *b*-axis and *c*-axis, respectively, at 4 and 80 K. The antiferromagnetic spin axis was in the direction of the *c*-axis for both compounds. However, the single crystal samples of FeV_2Se_4 partially twinned in the *c* plane. It may, therefore, be possible that the spin axis of FeV_2Se_4 is inclined from the *c*-axis toward the *a*-axis as well as FeV_2S_4, since both of

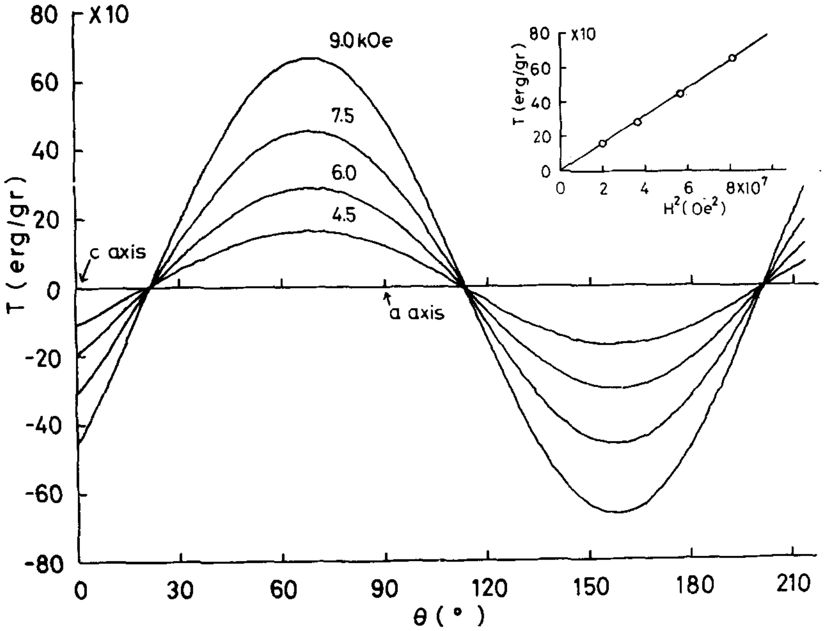

FIG. 5. Torque curves of FeV_2S_4 rotated along the *b*-axis at 4 K, together with the amplitude dependence on the square of the magnetic field.

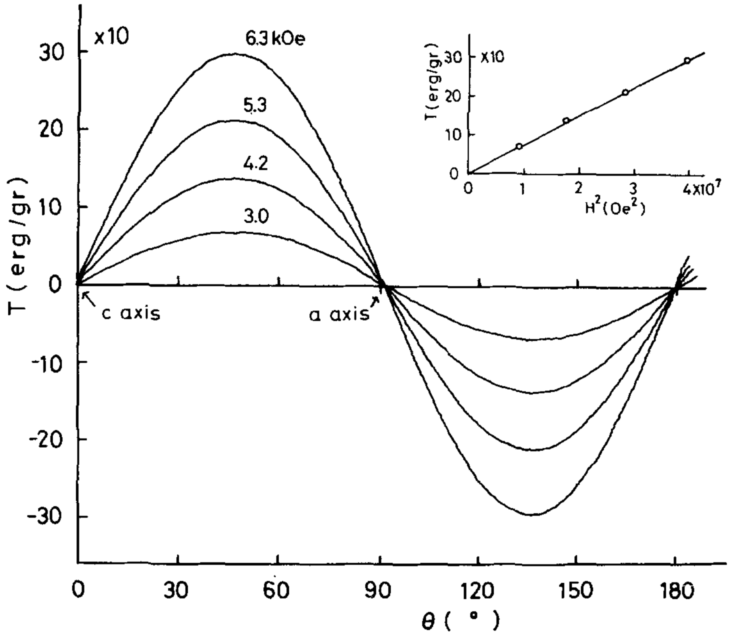

FIG. 6. Torque curves of FeV_2Se_4 rotated along the *b*-axis at 4 K, together with the amplitude dependence on the square of the magnetic field.

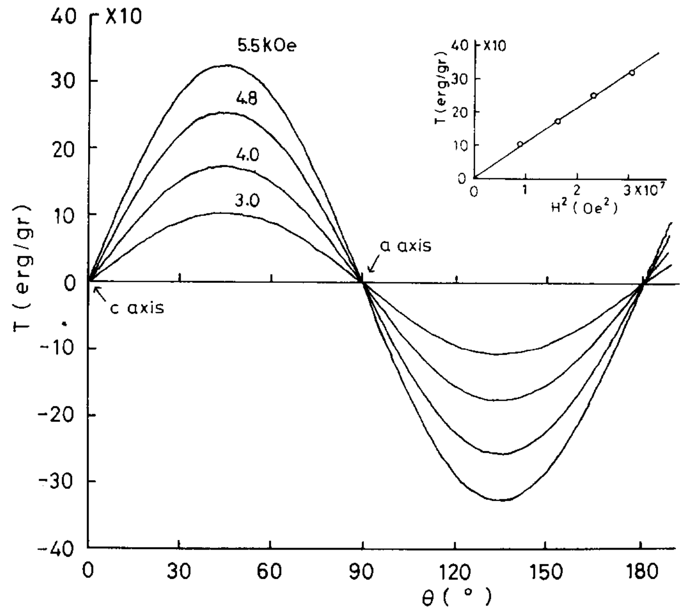

FIG. 7. Torque curves of Fe_2Se_4 rotated along the *b*-axis at 4 K, together with the amplitude dependence on the square of the magnetic field.

FeV_2S_4 and FeV_2Se_4 have the almost equal monoclinic angle of 92°. Figures 5 and 6 show the torque curves of FeV_2Se_4 and $FeTi_2Se_4$, respectively, rotated along the *b*-axis at 4 K. The torque amplitude changed linearly with the square of the magnetic field for both compounds.

3. *Susceptibility of the Single Crystal Samples*

The magnetic susceptibility of the single crystal samples of FeV_2S_4, FeV_2Se_4 and $FeTi_2Se_4$ was measured between 4 and 300 K. The measurements were carried out along the antiferromagnetic spin axis and perpendicular to it, based on the results of the torque measurements. The Néel point of the single crystals of FeV_2S_4, FeV_2Se_4 and $FeTi_2Se_4$ was 138, 100 and 133 K, respectively.

The susceptibility parallel and perpendicular to the spin axis in the *ac* plane for FeV_2S_4, FeV_2Se_4 and $FeTi_2Se_4$ is shown in Figs 8, 9 and 10, respectively. The other perpendicular susceptibility to the spin axis, along the *b*-axis, was also measured for all three compounds, and in agreement with that in the *ac* plane within ±5 %. The susceptibility had, therefore, uniaxial symmetry about the axis which nearly coincided with the direction of [101] for FeV_2S_4 and with the *c*-axis for FeV_2Se_4 and $FeTi_2Se_4$.

Below the Néel point parallel susceptibility for all three compounds was decreased with lowering temperature, while the perpendicular one gradually increased. The slight rise in the perpendicular susceptibility below about 10 K for all the compounds can probably be attributed to the small occlusion of the para-

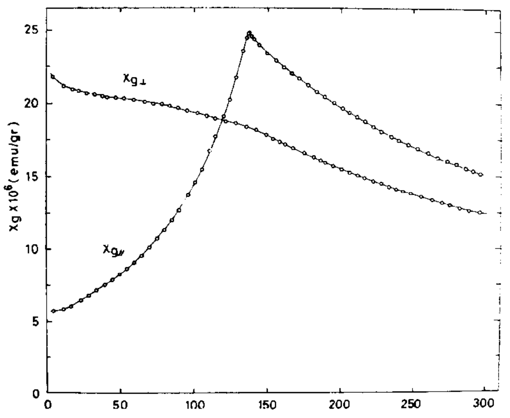

FIG. 8. Parallel and perpendicular susceptibility of FeV_2S_4.

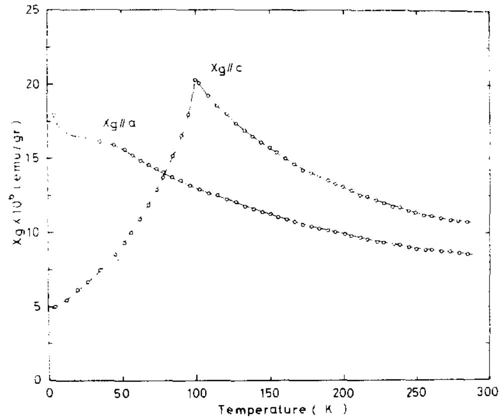

FIG. 9. Parallel and perpendicular susceptibility of FeV_2Se_4.

magnetic regions, such as the paramagnetic impurities or the partial disorder of vacancies. When extrapolated to 0 K, the parallel susceptibility of FeV_2S_4, FeV_2Se_4 and $FeTi_2Se_4$ was 5.7, 4.8 and 1.2 emu/g, respectively. According to the theory of antiferromagnetism, the parallel susceptibility in the antiferromagnetic ground state should be equal to 0. The residual parallel susceptibility of FeV_2S_4, FeV_2Se_4 and $FeTi_2Se_4$ can, therefore, be attributed to the paramagnetism of impurities or the temperature independent Pauli paramagnetism. The Pauli paramagnetism is likely to fairly contribute to the susceptibility of FeV_2S_4 and FeV_2Se_4, compared with that of $FeTi_2Se_4$. In fact the temperature independent paramagnetism of FeV_2S_4 and FeV_2Se_4 obtained from the powder measurements at high temperatures had a somewhat larger value than that of $FeTi_2Se_4$.

When the Curie–Weiss law was applied for the susceptibility above the Néel point, the paramagnetic moment and the paramagnetic Curie temperature were obtained. They are shown in Table II, together with the values of $FeTi_2S_4$ (*7*). The values in brackets are those from the uncorrected susceptibility for the temperature independent one.

The large anisotropy in the principal susceptibilities was observed even in the paramagnetic region for all the compounds. For example the parallel susceptibility of $FeTi_2Se_4$ was nearly twice as large as the perpendicular one at room temperature.

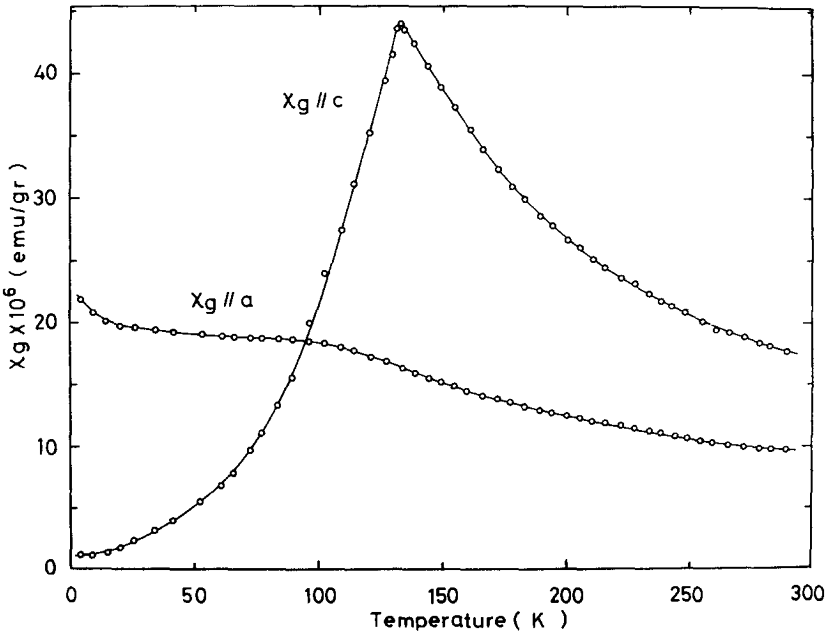

FIG. 10. Parallel and perpendicular susceptibility of $FeTiSe_4$.

TABLE II

PARAMAGNETIC MOMENTS AND PARAMAGNETIC CURIE TEMPERATURES OF FeV_2S_4, FeV_2Se_4 AND $FeTi_2Se_4$ FOR THE PARALLEL AND THE PERPENDICULAR SUSCEPTIBILITY TO THE SPIN AXIS, TOGETHER WITH THOSE OF $FeTi_2S_4$[a]

		P_{eff} (μ_B)	θ_p (K)
FeV_2S_4	$\chi_{\parallel}$	3.18 (3.81)	−62 (−120)
	$\chi_{\perp}$	2.96 (3.74)	−101 (−193)
FeV_2Se_4	$\chi_{\parallel}$	3.24 (3.86)	−55 (−88)
	$\chi_{\perp}$	3.20 (4.00)	−149 (−210)
$FeTi_2Se_4$	$\chi_{\parallel}$	4.00 (4.12)	+39 (+32)
	$\chi_{\perp}$	3.50 (3.71)	−72 (−91)
$FeTi_2S_4$	$\chi_{\parallel}$	3.95	+140
	$\chi_{\perp}$	3.45	+90

[a] Values in brackets are those from the uncorrected susceptibility for the temperature independent one.

The large magnetic anisotropy observed and the preference of the magnetic moments for the *c*-axis may be explained by the electronic state of iron atoms. The lowest term arising from ($3d^6$) configuration of the Fe^{2+} ion is D^5. Since the iron atoms are situated in the trigonally distorted octahedron of sulfur or selenium ions, there is the trigonal crystal field in addition to the main part of the cubic field. The fivefold orbital degeneracy is partially removed by the cubic crystal field, giving an orbital triplet and a doublet. The triplet lies lowest in energy. The trigonal crystal field splits this sublevel into a doublet and a singlet. The *d* orbitals in the ground state doublet mainly extend in the *c* plane, while that in the singlet in the direction of the trigonal *c*-axis. The *d* orbitals in the doublet are likely to somewhat overlap with those of the adjacent atoms in the *c* plane. The doublet state, therefore, seems to be lowered energetically by those overlapping, compared with the singlet state. In addition to the crystal fields, the spin-orbit interaction should be considered. When the lowest orbital doublet is well separated from the singlet as compared with the spin-orbit interaction, the magnetic moments favor the trigonal axis through the spin-orbit interaction, and the large anisotropy in the susceptibility parallel and perpendicular to the trigonal axis is expected, as theoretically studied by Kanamori (*10*). The magnetic anisotropy of $FeTi_2Se_4$ and $FeTi_2S_4$ would be explained by these arguments. However, the monoclinic distortion from the trigonal symmetry should not be disregarded for FeV_2S_4 and FeV_2Se_4.

Acknowledgments

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