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Magnetic Properties of Transition Metal–Rare-Earth Chalcogenide Spinels*

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Three transition metal–rare-earth chalcogenide spinels have been prepared by high-temperature solid-state reaction in evacuated sealed quartz tubes, and their magnetic susceptibilities determined as a function of temperature with Faraday apparatus. Results indicate that $MnYb_2S_4$ and $MnYb_2Se_4$ both contain divalent Mn and trivalent Yb, but $FeYb_2S_4$ appears to contain trivalent Fe and trivalent Yb. This may be explained on the basis of delocalization of one of the 3*d* electrons of Fe, which might be expected to make the compound an electrical conductor. Conductivity has indeed been experimentally observed in this compound, while the two Mn compounds are insulators. None of the data indicates long-range magnetic order in any of the compounds.

Introduction

The first rare-earth spinels reported (*1*) were of the type CdR_2X_4, where R represents the smaller rare earths and X is S or Se (e.g., $CdTm_2S_4$ and $CdDy_2Se_4$). Following this, there were reports of several other rare-earth thiospinels (*2*) and selenospinels (*3*), of which four contained a transition metal ion in addition to rare-earth ions with unpaired electrons. These compounds were $MnYb_2S_4$, $MnYb_2Se_4$, $FeYb_2S_4$, and $MnTm_2S_4$, all of which were found to be normal spinels, as are the cadmium rare-earth chalcogenide spinels. Because of the analogy between these compounds and the spinel ferrites, a study of their magnetic properties should have been in order, but to date, only one of them, $MnYb_2S_4$, has been so studied (*4*). The investigators found a magnetic moment corresponding to the presence of one Mn^{2+} and two Yb^{3+} ions per formula unit, and no evidence of long-range interaction. The selenospinel and the iron compound which were also available were not studied, but are included in the present paper.

Of the four compounds of interest, the authors of the present paper were able to prepare only three, $MnYb_2S_4$, $MnYb_2Se_4$, and $FeYb_2S_4$, and these were the compounds subjected to magnetic studies.

Preparation

All the ternary compounds were prepared by solid-state reaction between binary compounds. The required binaries (MnS, FeS, MnSe, Yb_2S_3, Yb_2Se_3, Tm_2S_3) were first prepared by reaction between stoichiometric quantities of pure metal turnings (Yb and Tm), powder (Mn), or wire (Fe), and elemental sulfur or selenium, in evacuated sealed quartz tubes. These reactions, which were of the solid-gas type, were carried out by raising the temperature slowly to 450°C, leaving it there for 4 hr, and then raising the temperature slowly again to 1000°C, and heating at that temperature for 16 hr more, after which cooling was effected rapidly by air-quenching. This procedure permits the reaction or most of it to occur at a rather low temperature in order to prevent reaction between the metals and the quartz. The more intense final heating assures completion of the reaction and uniformity of the product, which does not react with the quartz.

Following this, stoichiometric amounts of the binaries were thoroughly ground together and caused to react with each other in evacuated sealed quartz tubes for 18 hr, after which cooling was brought about by air-quenching. $MnYb_2S_4$ and $MnYb_2Se_4$ required only 1100°C for preparation while $FeYb_2S_4$ did not form until 1200°C. All three are, however, stable at 1200°C.

All binary and ternary compounds prepared were checked by X-ray diffraction to be certain that they had been properly formed.

Magnetic Measurements

The magnetic susceptibilities were determined by the Faraday method with apparatus consisting

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essentially of a 4-in. diameter Varian electromagnet with Faraday poles, along with a Cahn GRAM Electrobalance in a helium-filled glass chamber for measurement of weight change in the sample on application of magnetic fields. The magnet may be mechanically raised to and lowered away from the sample so that a Dewar flask with coolant can be inserted or removed. Samples of the order of 10 mg were employed and were placed in a 5-mm diameter quartz pan at the end of a quartz fiber in a Vycor hangdown tube. Weighings were first made without and then with the field applied at all temperatures. The field strength, H, in the vicinity of the sample was about 4 kG, and the constant force, $H\,dH/dx$, about 3.5 kG^2/cm.

Magnetic susceptibilities were calculated by comparison with results obtained in similar fashion at 20°C with an accepted standard, mercury thiocyanatocobaltate II ($Hg[Co(SCN)_4]$) (*5*) (Eastman Organic Chemicals #8588), whose gram susceptibility at 20°C is 16.44×10^{-6}.

A Cu-constantan thermocouple close to the sample pan was employed to measure temperature. All runs were made by starting at about 80°K (using liquid nitrogen as coolant) and slowly moving the coolant level away from the sample area by slowly boiling it off with a double-wound, insulated nichrome coil around the hangdown tube until room temperature was reached. Each compound was subjected to measurements twice, with different samples of the same preparation, and the results of the two runs are combined in the plots.

Results and Discussion

The experimental results are given in the $1/\chi_M$ vs T plots in Fig. 1. The $MnYb_2S_4$ results essentially confirm those of Longo and Raccah (*4*) in the temperature range common to the two studies, though our figures are somewhat higher. Since our minimum temperature was 80°K, we would be unable to see the departure from straight line behavior ascribed to Yb^{3+} at lower temperatures.

All three of the compounds studied in the present work have been found to obey the Curie–Weiss Law,

$$\chi_M = \frac{C_M}{T - \theta},$$

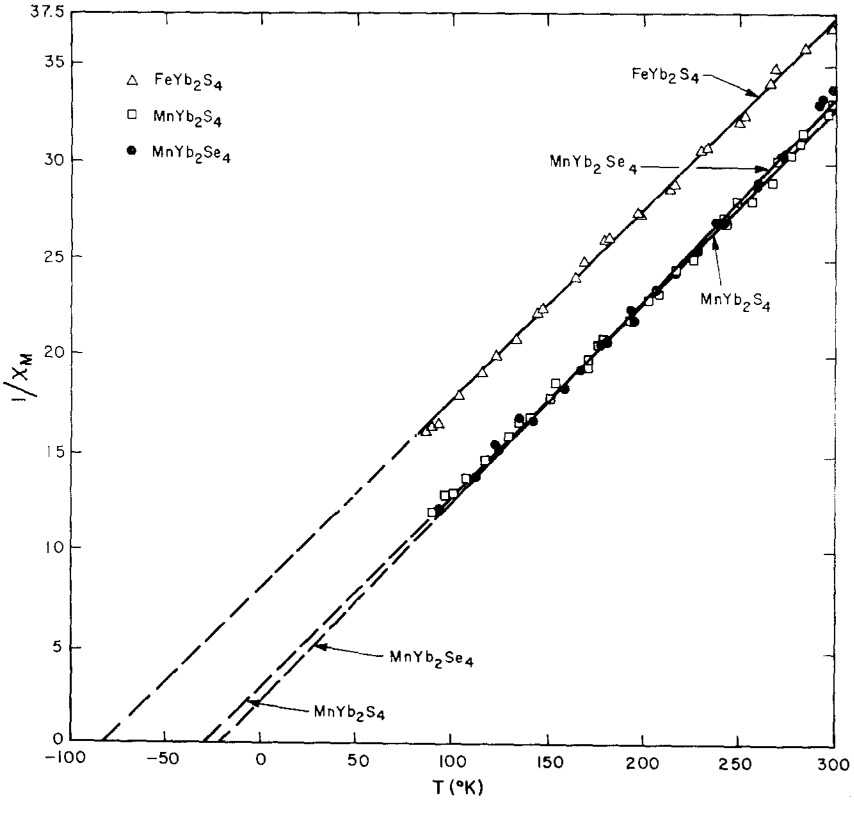

FIG. 1. Reciprocal molar susceptibility versus absolute temperature.

where χ_M is molar magnetic susceptibility, C_M the molar Curie constant, T the absolute temperature, and θ the Weiss constant. C_M values were calculated from measurements of the slopes of the three plots and θ by extrapolation to $1/\chi_M = 0$ (disregarding any possible unobserved change in slope at low temperature such as that reported in Ref. *4*).

The molar susceptibility, χ_M, is the sum of the gram-atom susceptibilities, and the molar Curie constant, C_M, the sum of the individual gram-atom Curie constants $[C_{M(\text{ind})}]$ of all atoms or ions in the formula unit of a compound. The individual gram-atom Curie constant for an atom or ion is related to the effective magnetic moment in Bohr magnetons, μ_{eff}, by the expression,

$$\mu_{\text{eff}} = 2.84\sqrt{C_{M(\text{ind})}},$$

which derives from the Langevin formula. Superimposed diamagnetic susceptibility is usually neglected and has been here.

Calculated values of μ_{eff} (in Bohr magnetons) of ions are obtained from the expression,

$$\mu_{\text{eff}} = g\sqrt{J(J+1)}.$$

For Yb^{3+}, the resulting calculated μ_{eff} and $C_{M(\text{ind})}$ are 4.54 and 2.58, respectively (*6*). For transition metal ions, J is often due to spin only so that

$$\mu_{\text{eff}} = g\sqrt{S(S+1)},$$

which with $g = 2$, yields theoretical values of 5.92 for Mn^{2+} and Fe^{3+}, and 4.90 for Fe^{2+}. The corresponding $C_{M(\text{ind})}$ values are therefore 4.34 for Mn^{2+} and Fe^{3+} and 2.98 for Fe^{2+}.

Table I summarizes all the magnetic data and calculations as well as some other observations. Lattice constants from X-ray diffraction powder patterns confirm that the spinels were those reported in Refs. (*2*, *3*). There is no evidence of long-range magnetic order in any of the compounds. The agreement between observed magnetic values and those calculated for the presence of one Mn^{2+} ion and two Yb^{3+} ions in both $MnYb_2S_4$ and $MnYb_2Se_4$ is good. However, $FeYb_2S_4$ is better explained by the presence of two Yb^{3+} ions along with one Fe^{3+} ion rather than an Fe^{2+} ion. Previous measurements of the magnetic moment of Fe^{2+} in various environments have indicated that the orbital contribution cannot be neglected; that is, that the observed moment and corresponding $C_{M(\text{ind})}$ values are 5.0–5.5 (*7*) and 3.10–3.75, respectively, rather than the spin-only values of 4.90 and 2.98, respectively. However, the *highest* possible expected C_M value for $Fe^{2+}Yb_2^{3+}S_4$ would then still be only 8.91 while the observed value is 10.3_4, which is then 16% high, compared with corresponding 4% and 7% figures for $MnYb_2Se_4$ and $MnYb_2S_4$, respectively. The measured value is 27% higher than the C_M value of 8.14 calculated with the use of the spin-only value for Fe^{2+}. The difference between the 4–7% and the 16–27% ranges is clearly significant; assumption of the presence of one Fe^{3+} ion and two Yb^{3+} ions yields a calculated C_M of 9.50, in which case the experimental result is only 9% high—a figure more in line with those obtained with the Mn compounds.

If the iron were present in trivalent form along with one Yb^{2+} and one Yb^{3+} ion, the calculated C_M would be 6.92 so that the observed value would be even more unreasonable. The results therefore suggest that one $3d$ electron of iron is delocalized, in which case the material could be an electrical conductor. Simple qualitative tests at room temperature with an ohmmeter to measure resistance between probes touching a sample pellet (formed from powder with a piston-and-cylinder die in a hydraulic press) have shown that this compound does indeed exhibit some conductivity, while $MnYb_2S_4$ and $MnYb_2Se_4$ are insulators. The level of conductivity appears to be quite low, however, so that, if there is one free electron per formula unit, the mobility is very low.

TABLE I

MAGNETIC DATA AND CALCULATIONS, AND SOME OTHER OBSERVATIONS

Compound	Body Color	Lattice Constants, a (Å) Present Work (±0.01 Å)	Refs. (*2*, *3*)	$C_{M(\text{exp})}$	C_M(calcd for $M^{2+} + 2Yb^{3+}$)	θ (°K)
$MnYb_2S_4$	Yellow-green	10.95	10.949 ± 0.006	10.1_5	9.50	−30
$MnYb_2Se_4$	Very dark brown	11.42	11.42 ± 0.01	9.8_5	9.50	−23
$FeYb_2S_4$	Black	10.83	10.838 ± 0.006	10.3_4	8.14	−83

Kugimiya and Steinfink (*8*) have devised the following formula for calculating approximate lattice constants of spinels:

$$a_{\text{calcd}} = \tfrac{1}{2}[\text{calcd cell edge}] + \tfrac{1}{2}\left[\frac{\text{calcd face diagonal}}{\sqrt{2}}\right]$$
$$= \tfrac{1}{2}[4(r_{\text{oct}} + r_{\text{an}})] + \tfrac{1}{2}\left[\frac{4(r_{\text{tet}} + r_{\text{an}})\sqrt{2}/\sqrt{3} + 4r_{\text{an}}}{\sqrt{2}}\right],$$

where r_{oct} = Radius of cation on octahedral site;
r_{tet} = Radius of cation on tetrahedral site;
r_{an} = Radius of anion.

Substituting in this formula Ahrens' radii for Yb^{3+} (0.86 Å), Mn^{2+} (0.80 Å), Fe^{2+} (0.74 Å), and Fe^{3+} (0.64 Å); and Pauling's radii for S^{2-} (1.84 Å) and Se^{2-} (1.98 Å), one obtains the calculated values given in Table II. Also in Table II are the experimental values and those calculated using the Kugimiya–Steinfink approach but giving two-thirds weight in the average (rather than one-half) to the value calculated from the cell edge because this expression deals with the octahedral ions (of which there are 16 per unit cell), and only one-third weight to the value calculated from the face diagonal because it deals with tetrahedral ions (of which there are only eight). Although the formula used cannot necessarily be expected to provide extremely accurate predictions, and one must be concerned about the validity of radii used for ions in given environments, chiefly where there may be a covalent contribution, this analysis seems to be reasonable, especially for the sulfides, and does, therefore, again appear to indicate the presence of Fe^{3+} rather than Fe^{2+} ions. Determination of the valence by other available methods appears desirable.

TABLE II

OBSERVED AND CALCULATED LATTICE CONSTANTS

Proposed Formulas	Lattice Constants, *a* (Å) Observed	Calculated by Method in Ref. (8)	Calculated by Modification of Method in Ref. (8)
$Fe^{2+}Yb_2^{3+}S_4$	10.83	10.98	10.92
$Fe^{3+}Yb_2^{3+}S_4$		10.87	10.84
$Mn^{2+}Yb_2^{3+}S_4$	10.95	11.05	10.97
$Mn^{2+}Yb_2^{3+}Se_4$	11.42	11.69	11.58

References

1. L. SUCHOW AND N. R. STEMPLE, *J. Electrochem. Soc.* **110**, 187C (1963); **111**, 191 (1964).
2. M. PATRIE, J. FLAHAUT, AND L. DOMANGE, *C. R. Acad. Sci. Paris* **258**, 2585 (1964).
3. M. GUITTARD, C. SOULEAU, AND H. FARSAM, *C. R. Acad. Sci. Paris* **259**, 2847 (1964).
4. J. M. LONGO AND P. M. RACCAH, *Mater. Res. Bull.* **2**, 541 (1967).
5. B. N. FIGGIS AND R. S. NYHOLM, *J. Chem. Soc. London*, 4190 (1958).
6. S. KERN AND P. M. RACCAH, *J. Phys. Chem. Solids* **26**, 1625 (1965).
7. P. W. SELWOOD, "Magnetochemistry," 2nd ed., p. 159, Interscience Publishers, Inc., New York, 1956.
8. K. KUGIMIYA AND H. STEINFINK, *Inorg. Chem.* **7**, 1762 (1968).