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# Structure and Magnetic Properties of Sulfides of the Type Cd$RE_2S_4$ and Mg$(Gd_xYb_{1-x})_2S_4$

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Cd$RE_2S_4$ ($RE$ = Gd, Tb, Dy, Ho, Er, Tm, and Yb) and Mg$(Gd_xYb_{1-x})_2S_4$ were prepared by solid-state reactions. All the cadmium-containing compounds are cubic, i.e., the $Th_3P_4$ structure for Gd, Tb, and Dy and the spinel type for all the others. The first three compounds were deficient in CdS. In the case of the Mg system, for $x = 1$ the system is cubic $Th_3P_4$, for $x = 0$ cubic spinel, and for $0 < x < 1$ orthorhombic $MnY_2S_4$ ($Cmc2_1$). All the materials studied are paramagnetic above 77 K. Below 77 K in the magnesium family both cubic materials are paramagnetic down to 4.2 K and the orthorhombic materials show magnetic ordering. In the cadmium family all but $CdTm_2S_4$ show exchange coupling.

## Introduction

The cubic spinel structure is found for many compounds with the general formula $ARE_2S_4$, especially where $A$ = Cd and $RE$- = rare earth. The nonmagnetic ion cadmium is rather large and to a good approximation $r(Cd^{2+})/r(RE^{3+}) \simeq 1$ where $r$ denotes the ionic radius. The study of the magnetic properties of Cd$RE_2S_4$ is comparatively simple because only the lanthanide is magnetic and because the structure remains very nearly unchanged due to the constancy in the radius ratio of cadmium : lanthanide. Flahaut and his colleagues (*1*, *2*) devoted much time and thought toward the preparation and the solution of the crystal structure of a large variety of chalcogenides, among them the Cd$RE_2S_4$ materials. However, Suchow and Stemple (*3*) were the first to prepare and recognize the existence of rare earth spinels and list their *d*-spacings, e.g., $CdY_2S_4$ which was unidentified by Flahaut's group (*4*). Some more compounds of the type Cd$RE_2S_4$ and Cd$RE_2Se_4$, where $RE$ are the heavy lanthanide ions, were patented by Suchow (*5*). Some of these compounds were also reported by Holtzberg (*6*). Suchow and Stemple (*3*) also found the cubic $Th_3P_4$ structure for $CdGd_2Se_4$ and $EuGd_2Se_4$ and gave their lattice constants. They declared that "rare earths of small ionic size will yield spinel, those of somewhat larger size the $Th_3P_4$ structure, and the largest no ternary compounds at all." Fujii *et al.* (*7*) reported crystallographic and magnetic data on $CdHo_2S_4$, $CdEr_2S_4$, and other Cd$RE_2Se_4$ compounds. Yim *et al.* (*8*) studied not only the structure and cell parameters but also semiconductor and cathodoluminescence properties of Cd$RE_2S_4$ and other similar compounds. Pokrzywnicki *et al.* studied, among others, the magnetic

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properties of two of the spinels, e.g., $CdTm_2S_4$ (*9*) and $CdYb_2S_4$ (*10*). Lugscheider *et al.* (*11*) studied a family of $EuRE_2S_4$ and $CdGd_2S_4$ compounds for comparison.

Magnesium is smaller than cadmium so that $r(Mg^{2+})/r(RE^{3+}) < 1$, the ratio varying with the size of the lanthanide, and the structure of $MgRE_2S_4$ will change even when $r(RE^{3+})$ changes by less than 10%, i.e., in going from $Gd^{3+}$ to $Yb^{3+}$. Both $MgYb_2S_4$ (*12*) with cubic spinel type and $MgGd_2S_4$ (*13*) with cubic $Th_3P_4$ structure had been studied. Both materials being cubic were expected to be nonmagnetically ordered, but their solid solutions containing Gd and Yb were expected to be noncubic and, as a result, to show some magnetic ordering.

Thus the present research was planned with the aim of studying the magnetic behavior of the lanthanides in the series $CdRE_2S_4$ on the one hand and in the $Mg(Gd_xYb_{1-x})_2S_4$ solid solution system on the other hand, whereby the metal ion (Cd or Mg) is always nonmagnetic and the lanthanides change either with atomic number from Gd to Yb or with different weight ratios of Gd and Yb.

## Experimental and Results

### *Preparation of Samples*

The sulfides, $RE_2S_3$, were prepared by heating Research Chemicals 99.9% oxides in a stream of $CS_2$ at 1000°C for 12 hr. The other sulfides, CdS and MgS, were obtained from ultrapure Ventron Alfa Products and Merck >99.5%, respectively. The appropriate metal sulfides in stoichiometric amounts were ground, mixed, and introduced into a quartz ampoule. The ampoule was evacuated, sealed, and heated at 1100°C for 48 hr. After quenching, the ampoule was broken open and chemical analyses for magnesium and cadmium were carried out by atomic absorption spectrometry. The error in the determination of the metal was to within 1%. Some of the cadmium materials obtained were nonstoichiometric and one was impure as will be discussed below.

### *Structure*

In some cases more than one phase was observed by X-ray diffraction. In the materials containing Ho or Er, two distinct phases were identified and they could be separated by hand under the microscope owing to different habit and hue. The materials were identified as $CdHo_4S_7$ and $CdHo_2S_4$, and $CdEr_4S_7$ and $CdEr_2S_4$, respectively. The former in each case was monoclinic of type $FeY_4S_7$ (*14, 15*) and the latter cubic spinel (*1*). In the case of Dy the two phases, viz. $CdDy_4S_7$ (type $FeY_4S_7$) and $CdDy_2S_4$ (type $Th_3P_4$), were interdispersed and could not be readily separated. For Tm and Yb only one spinel phase, viz. $CdTm_2S_4$ and $CdYb_2S_4$ were obtained. In the latter case some excess $Yb_2S_3$ was found alongside the spinel phase. The two other lanthanides, Gd and Tb, gave also only one phase, $Th_3P_4$, but the compounds were not stoichiometric. There was always a deficiency in CdS, and the reaction taking place could be formulated as follows:

$$CdS + RE_2S_3 \rightarrow \frac{3}{3+x} Cd_{1-x}RE_{2+2x/3}S_4 + \frac{4x}{3+x} CdS.$$

Some of the volatile CdS accumulated in these cases in the comparatively cooler parts of the sealed tube. Chemical analyses and magnetic susceptibility gave the following stoichiometries: $Cd_{0.5}Gd_{2.3}S_4$ and $Cd_{0.4}Tb_{2.4}S_4$. Table I gives the cell parameters and the $R$ discrepancy factor, defined as:

$$R = \frac{\Sigma |I_{obs} - I_{calc}|}{\Sigma I_{obs}} \times 100,$$

for various cadmium compounds compared

TABLE I

X-RAY DATA FOR Cd$RE_2$S$_4$, $RE$ = Gd TO Yb[a]

|  | $R$% | $a_0$ | $a_0$(*6*) | $a_0$(*8*) | $a_0$(*9, 10*) | $a_0$(Ref.) | Structure |
|---|---|---|---|---|---|---|---|
| Cd$_{0.5}$Gd$_{2.3}$S$_4$ | — | 8.368 |  |  |  |  | Th$_3$P$_4$ |
| Cd$_{0.4}$Tb$_{2.4}$ S$_4$ | 9.7 | 8.343 |  |  |  |  | Th$_3$P$_4$ |
| Cd Dy$_2$ S$_4$ | — | 2 phases |  |  |  |  | Th$_3$P$_4$ |
| Cd Ho$_2$ S$_4$ | 12.3 | 11.167 | 11.168 | 11.1674 |  | 11.240(*7*) | Spinel |
| Cd Er$_2$ S$_4$ | 10.4 | 11.128 | 11.136 | 11.1347 |  | 11.192(*7*) | Spinel |
| Cd Tm$_2$ S$_4$ | 13.4 | 11.097 | 11.092 | 11.09 | 11.10 | 11.092(*3*) | Spinel |
| Cd Yb$_2$ S$_4$ | containing Yb$_2$S$_3$ | 11.043 | 11.068 | 11.068 | 11.066 |  | Spinel |

[a] $a_0$ in Å.

to those reported in the literature. The first two columns show the values obtained in this study. In one case, CdEr$_2$S$_4$, single crystals were grown and the crystal structure was fully solved (*16*). Flahaut (*1*) and also Yim *et al.* (*8*) reported the cubic Th$_3$P$_4$ structure for the cadmium gadolinium compound but neither stoichiometry nor cell parameters were published. Lugscheider *et al.* (*11*) reported the cell parameter ($a_0$ = 8.38 Å) for the same compound but gave no experimental details. Suchow and Stemple (*3*) gave observed and calculated intensities for CdTm$_2$S$_4$, with an $R$ factor of 5.8–7.8% indexed for normal spinel.

In the solid solution system, Mg(Gd$_x$Yb$_{1-x}$)$_2$S$_4$, the coordination number and accordingly the structure changes as a function of $x$, i.e., MgGd$_2$S$_4$ is cubic Th$_3$P$_4$ (C.N. = 8 and 8), MgYb$_2$S$_4$ is cubic spinel (C.N. = 4 and 6), and the mixed lanthanide solid solutions are orthorhombic MnY$_2$S$_4$ (C.N. = 6 and 6). The cell parameters are given in Table II. Detailed X-ray data for MgGd$_2$S$_4$ were published elsewhere (*17*). The cell parameter $a_0$ of MgYb$_2$S$_4$ observed by Patrie *et al.* (*12*) was 10.957 Å, very close to the value reported by us.

### *Magnetic Measurements*

In the high-temperature range (77–300 K) all the Cd$RE_2$S$_4$ materials studied were paramagnetic. The magnetic data for this temperature range are shown in Table III.

For low temperatures all but CdTm$_2$S$_4$ (Fig. 1) show some magnetic ordering, the strongest effect appearing for CdEr$_2$S$_4$. Thus in a plot of magnetization vs field

TABLE II

X-RAY DATA FOR Mg(Gd$_x$Yb$_{1-x}$)$_2$S$_4$[a]

|  | $x$ | $a_0$ | $b_0$ | $c_0$ | Structure |
|---|---|---|---|---|---|
| MgGd$_2$S$_4$ | 1.0 | 8.359 |  |  | Cubic Th$_3$P$_4$ |
| MgGd$_{1.75}$Yb$_{0.25}$S$_4$ | 0.875 | 3.78 | 12.73 | 12.58 | Orthorhombic MnY$_2$S$_4$ |
| MgGd$_{1.5}$ Yb$_{0.5}$ S$_4$ | 0.75 | 3.77 | 12.72 | 12.57 | Orthorhombic MnY$_2$S$_4$ |
| MgGd$_{1.0}$ Yb$_{1.0}$ S$_4$ | 0.50 | 3.75 | 12.70 | 12.55 | Orthorhombic MnY$_2$S$_4$ |
| MgGd$_{0.5}$ Yb$_{1.5}$ S$_4$ | 0.25 | 3.74 | 12.69 | 12.54 | Orthorhombic MnY$_2$S$_4$ |
| MgGd$_{0.25}$Yb$_{1.75}$S$_4$ | 0.125 | 3.74 | 12.68 | 12.53 | Orthorhombic MnY$_2$S$_4$ |
| MgYb$_2$S$_4$ | 0.0 | 10.967 |  |  | Cubic Spinel |

[a] Cell parameters in Å.

TABLE III

EFFECTIVE MOMENT $\mu$(B.M.) AND CURIE TEMPERATURE $\theta$(K) OF Cd$RE_2S_4$

|  | $\mu_{\text{obs}}$ | $\mu_{\text{calc}}$ | $-\theta$ | $\mu$(Ref.) |
|---|---|---|---|---|
| $Cd_{0.5}Gd_{2.3}S_4$ | 7.8 | 7.9 | 8 |  |
| $Cd_{0.4}Tb_{2.4}S_4$ | 9.8 | 9.7 | 15 |  |
| Cd $Ho_2$ $S_4$ | 10.3 | 10.6 | 10 | 10.7(7) |
| Cd $Er_2$ $S_4$ | 9.6 | 9.6 | 9 | 9.8(7) |
| Cd $Tm_2$ $S_4$ | 7.5 | 7.6 | 16 | 7.6(9) |
| Cd $Yb_2$ $S_4$ | 4.9 | 4.5 | 74 |  |

strength at 4.2 K one observes a straight line of moderate slope for $CdTm_2S_4$, a steep curved line for $CdEr_2S_4$, and the rest with intermediate behavior. The difference between $CdEr_2S_4$ and $CdTm_2S_4$ is also well demonstrated in Fig. 2 which depicts the magnetization $M$(EMU/mole) and reciprocal molar susceptibility vs temperature for the two compounds, i.e., $CdEr_2S_4$—top figure, $CdTm_2S_4$—bottom figure. Whereas the magnetization rises steeply for $CdEr_2S_4$ and has appreciably higher values, e.g., reaching $32 \cdot 10^3$ for low temperatures and high field, the magnetization barely varies with temperature for $CdTm_2S_4$ and the values of $M$ are smaller.

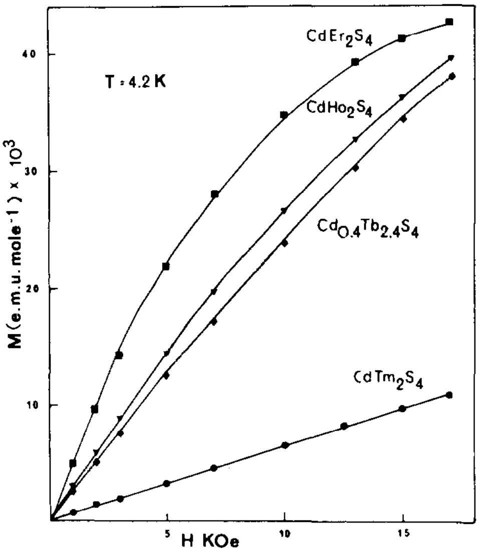

FIG. 1. Magnetization against magnetic field for some Cd$RE_2S_4$ at 4.2 K.

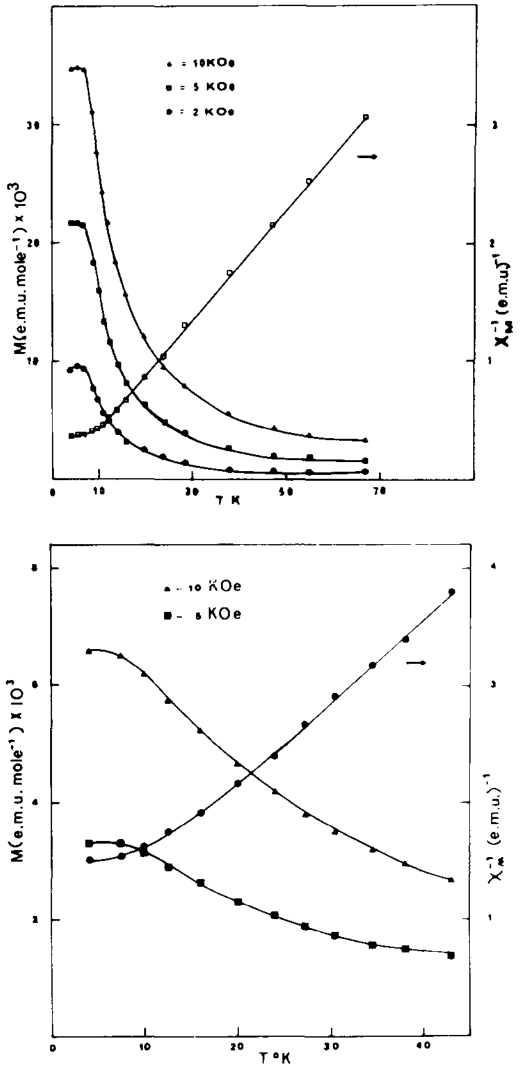

FIG. 2. Magnetization and reciprocal susceptibility against temperature for different field strengths for $CdEr_2S_4$ (top) and $CdTm_2S_4$ (bottom).

In the case of the solid solution system, $Mg(Gd_xYb_{1-x})_2S_4$ paramagnetism is observed for all materials above 77 K. The magnetic data are given in Table IV.

Magnetization vs field for both pure components, $MgGd_2S_4$ and $MgYb_2S_4$, is linear, and all the orthorhombic $MnY_2S_4$-type ma-

TABLE IV

CURIE CONSTANT, $C$, AND CURIE TEMPERATURE $\theta$(K) FOR $Mg(Gd_xYb_{1-x})_2S_4$

| | $x$ | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1.0 | 0.875 | 0.75 | 0.50 | 0.25 | 0.125 | 0.0 |
| $C_{obs_x}$ | 15.8 | 14.5 | 13.4 | 10.4 | 8.0 | 6.7 | 5.9 |
| $C_{calc_x}$ | 15.6 | 14.3 | 13.0 | 10.4 | 7.7 | 6.4 | 5.1 |
| $-\theta$ | 10.6 | 3.2 | 6.0 | 6.8 | 21.0 | 35.0 | 81.0 |

terials show curved variations (Figs. 3a and b). The magnetic behavior of one of the latter materials viz. $MgGdYbS_4$ ($x = 0.50$), against temperature is presented as an example in Fig. 4. The others are quite similar.

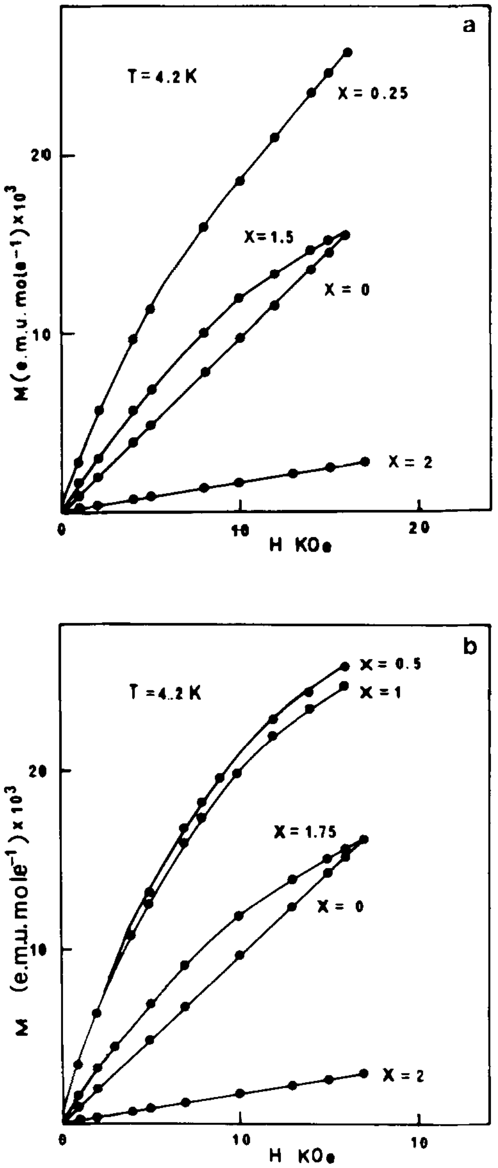

FIG. 3. (a, b): Magnetization against field for $Mg(Gd_{2-x}Yb_x)S_4$ at 4.2 K (shown in two parts for clarity).

## Discussion

Although there were experimental difficulties in obtaining Cd*RE*$_2$S$_4$ materials owing to the volatility of CdS, most of them were eventually prepared, analyzed, and their crystal structure determined. Also, an acceptable discrepancy *R* factor was obtained (≈10%) for powdered samples showing that the site occupancy was that of $Th_3P_4$ for the rare earths Gd, Tb, and Dy and normal spinel for all others. No evidence for an inverse spinel was found as reported for $CdHo_2S_4$ by Fujii *et al.* (*7*). There are, in fact, no known compounds of spinel type with lanthanide ions in tetrahedral sites. If an inverse spinel could exist for Cd*RE*$_2$S$_4$ compounds, it should prefer the *smaller* lanthanide ions rather than the larger ones, i.e., a situation opposed to the postulates of Fujii *et al.* (*7*) and Pokrzywnicki and Czopnik (*9*). The contraction of the radii is less than 10% in going from Gd to Lu. Thus there is a close similarity in ionic radius and electronegativity between the neighboring Dy and Ho, yet the former prefers C.N. = 8 ($Th_3P_4$) and the latter coordination 6 (spinel). This abrupt change cannot be explained solely by Steinfink's (*18, 19*) model, which is based mainly on changes in the two parameters of radius and electronegativity. It could of course be dependent on ratios of the ionic radii $r(Cd^{2+})/r(RE^{3+})$ similar to Pauling's geometrical laws for closest-packed structures.

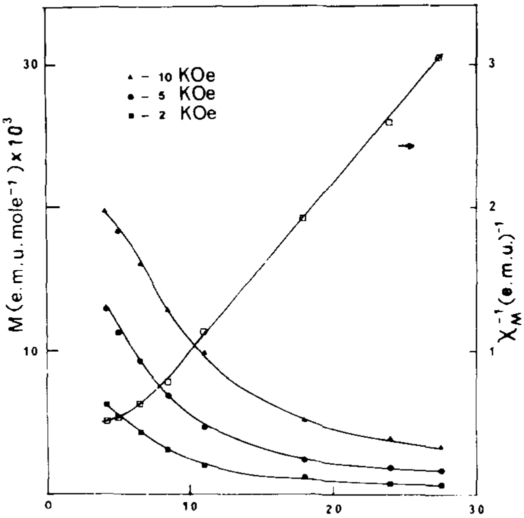

FIG. 4. Magnetization and reciprocal susceptibility against temperature for various field strengths for $MgGdYbS_4$.

Concerning the magnetic behavior, $CdTm_2S_4$ obeyed the Curie–Weiss law down to low temperatures. However, below 15 K a nearly temperature-independent paramagnetism (TIP) could be observed. The ion $Tm^{3+}$ ($f^{12}$) has a ground state $^3H_6$ which splits in a cubic field to singlets and triplets. The lowest level is a (nonmagnetic) singlet and interaction between this level and higher lying triplets results in TIP. This behavior was also observed by Pokrzywnicki and Czopnik (*9*). For $CdHo_2S_4$ there is a similar behavior. This $f^{10}$ ion ($^5I_8$) also splits into various Stark levels, the lowest one being a singlet. Here again TIP occurs from interaction between the lowest level and a higher one. The (average) exchange integral can be calculated (*20*) for both compounds and was found to be 0.76 and 0.15 K, respectively, thus showing that the antiferromagnetic superexchange coupling is very weak. The behavior of $Cd_{0.4}Tb_{2.4}S_4$ is very similar to that of $CdHo_2S_4$. This $f^8$ ion ($^7F_6$) has Stark levels similar to those of $Tm^{3+}$. It does not necessarily have the same order of levels since the point symmetry of the lanthanide ion in the $Th_3P_4$ structure is very different from that in the spinel structure but since the magnetic behavior is similar it is assumed that there, too, TIP behavior exists. The treatment is different for the case of $CdGd_2S_4$, studied also by Lugscheider *et al.* (*11*). The lanthanide ion here is an S ion ($f^7$–$^8S_{7/2}$) and thus not affected at all by the crystal field so that TIP is either nonexistent or can be ignored. Comparing the curves of $\chi^{-1}$ vs $T$ for $CdGd_2S_4$, $EuLa_2S_4$, and $EuGd_2S_4$ which are isomorphous compounds, the conclusion is that an antiferromagnetic coupling Gd–Gd exists. The two ions, $Er^{3+}$ ($f^{11}$) and $Yb^{3+}$ ($f^{13}$), are Kramers ions as well, so that the ground levels are magnetic doublets and not singlets. Thus the behavior of $\chi^{-1}$ vs $T$ in the low-temperature region might be due to the role of these doublets and the existence of negative superexchange coupling for both Er–Er and Yb–Yb. An analysis of the magnetic susceptibility for $CdYb_2S_4$ by means of the crystal field method was discussed by Pokrzywnicki (*10*).

Fujii *et al.* (*7*) studied $CdHo_2S_4$ and $CdEr_2S_4$. They claimed the structure to be a partially inverse spinel and assumed positive exchange interaction between the lanthanide ions in the tetrahedral and octahedral sites. While this structure was not confirmed in our study, they also found the saturation moment for Er considerably smaller (5.4 B.M./atom) than the theoretical one (9.0 B.M./atom), which they attributed to partial quenching of the moment by the crystal field. In this study a similar difference was observed (4.6 B.M./atom as opposed to 9.6 B.M./atom), but that could be due to magnetic superexchange coupling rather than ferromagnetism.

In brief, in $CdRE_2S_4$ compounds, the non-Kramers ions (Tb, Ho, and Tm) are TIP at low temperatures, while the Kramers ions (Gd, Er, and Yb) show negative cooperative phenomena.

When a solid solution $MgRE'RE''S_4$ is

TABLE V

RADII (Å) ACCORDING TO SHANNON COMPARED TO AVERAGE RADII, $\bar{r}$, FOR $Mg(Gd_xYb_{1-x})S_4$

| | $Gd^{3+}$ | $Tb^{3+}$ | $Dy^{3+}$ | $Ho^{3+}$ | $Er^{3+}$ | $Tm^{3+}$ | $Yb^{3+}$ |
|---|---|---|---|---|---|---|---|
| $r$ | 1.14 | 1.12 | 1.11 | 1.098 | 1.085 | 1.077 | 1.065 |
| $x$ | 0.95 | 0.875 | 0.75 | 0.50 | 0.25 | 0.125 | 0.05 |
| $\bar{r}$ | 1.136 | 1.130 | 1.121 | 1.102 | 1.084 | 1.074 | 1.068 |

formed from two very different lanthanide ions such as $Gd^{3+}$ and $Yb^{3+}$, it is possible to visualize the existence of an imaginary lanthanide ion having an average radius of the two ions. Thus it is possible to compare these average (calculated) radii, $\bar{r}$, with the radii of lanthanides (in coordination number 7[2]) as given by Shannon *et al.* (*21*). This comparison is shown in Table V.

From Table V it can be seen that the average radii obtained are indeed quite similar to the radii of the individual lanthanide ions. The ions lying between $Tb^{3+}$ and $Tm^{3+}$ form with $Mg^{2+}$ a series of orthorhombic-type $MnY_2S_4$ compounds with the general formula $MgRE_2S_4$ (*22*).[3] Thus it was not surprising that Mg gave the same type compounds with the pair Gd–Yb for $0.875 \geq x \geq 0.125$. For $x = 0.95$ and 0.05, it was impossible to obtain a single phase material; for the former a mixed cubic $Th_3P_4$ and orthorhombic $MnY_2S_4$ phase was obtained (cf. $MgGd_2S_4$) and for the latter a cubic spinel–orthorhombic $MnY_2S_4$ phase (cf. $MgYb_2S_4$). The correlation between average radius and structure is striking because the crystal contains in fact two randomly distributed ions differing in radius by about 7%!

The cubic structures showed no magnetic ordering. However, as was expected for the lower symmetry orthorhombic solid solutions, cooperative phenomena were observed. Now, both $Gd^{3+}$ and $Yb^{3+}$ are Kramers ions having magnetic doublets as the lowest Stark levels. Thus the magnetic behavior might be due to a superexchange (probably weak) between the metal ions via the sulfide ion. The extrapolated saturation moment is rather low and might be due to the angle between the two lanthanide ions and the sulfur ion which differs from 180°.

Thus the system $Mg(Gd_xYb_{1-x})_2S_4$ behaves as if it were the system $Mg\overline{RE}_2S_4$ where $\overline{RE}$ is an imaginary lanthanide with the average ionic radius (and properties?) of Gd and Yb. Mössbauer effect studies, optical and EPR methods, could be helpful for a more detailed discussion.

## References

1. J. FLAHAUT, *in* "Progress Sci. Technol. Rare Earths" (L. Eyring, Ed.), Vol. III, Chap. 6, pp. 209–283. Pergamon, Oxford (1968).
2. J. FLAHAUT, M. GUITTARD, M. PATRIE, M. P. PARDO, S. M. GOLABI, AND L. DOMANGE, *Acta Cryst.* **19,** 14 (1965).
3. L. SUCHOW AND N. R. STEMPLE, *J. Electrochem. Soc.* **110,** 187C (1963); **111,** 191 (1964).
4. J. FLAHAUT, L. DOMANGE, AND M. PATRIE, *Bull. Soc. Chim. France* No. 35, 159 (1962).
5. L. SUCHOW, U.S. Patent #3,174,939 (1965).
6. F. HOLTZBERG, privately communicated to Flahaut; cf. ref. *1*, see also *Acta Cryst.* **16,** A44 (1963).
7. H. FUJII, T. OKAMOTO, AND T. KAMIGAICHI, *J. Phys. Soc. Japan* **32,** 1432 (1972).
8. W. M. YIM, A. K. FAN, AND E. J. STOFKO, *J. Electrochem. Soc.* **120,** 441 (1973).
9. S. POKRZYWNICKI AND A. CZOPNIK, *Phys. Stat. Sol.* **b70,** K85 (1975).
10. S. POKRZYWNICKI, *Phys. Stat. Sol.* **b71,** K111 (1975).
11. W. LUGSCHEIDER, H. PINK, K. WEBER, AND W. ZINN, *Z. Angew Phys.* **30,** 36 (1970).
12. M. PATRIE, J. FLAHAUT, AND L. DOMANGE, *C.R. Acad. Sci. Paris* **258,** 2585 (1964).
13. I. SHILO, Thesis, Jerusalem, (1979).

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[2] Coordination 7 was chosen as a mean between the lanthanide coordination existing in the various structures of this solid solution.

[3] An exception should be mentioned: In the case of $MgTm_2S_4$, two phases coexist: cubic spinel and orthorhombic $MnY_2S_4$ type, and special conditions of preparation are needed to get one pure phase.

14. A. Adolphe, *Ann. Chim.* **10,** 271 (1965).
15. A. Adolphe and P. Laruelle, *Bull. Soc. Fr. Mineral. Cristallogr.* **91,** 219 (1968).
16. A. Tomas, I. Shilo, and M. Guittard, *Mat. Res. Bull.* **13,** 857 (1978).
17. L. Ben-Dor and I. Shilo, *J. Solid State Chem.* **35,** 103 (1980).
18. K. Kugimiya and H. Steinfink, *Inorg. Chem.* **7,** 1762 (1968).
19. J. E. Iglesias and H. Steinfink, *J. Solid State Chem.* **6,** 119 (1973).
20. J. R. Mignod, R. Ballestracci, S. Quezel, C. Linares, and F. Tcheon, *J. Phys. Chem. Solids* **30,** 2679 (1969).
21. R. D. Shannon and C. T. Prewitt, *Acta Cryst.* **B25,** 925 (1969).
22. M. Patrie and M. R. Chevalier, *C.R. Acad. Sci. Paris* **263C,** 106 (1966).