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SYNTHESIS OF RARE EARTH COMPOUNDS  
AND STUDY OF THEIR MAGNETIC OPTICAL  
AND SEMICONDUCTING PROPERTIES

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IBM Thomas J. Watson Research Center

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IBM Corporation  
Thomas J. Watson Research Center  
Yorktown Heights, New York 10598

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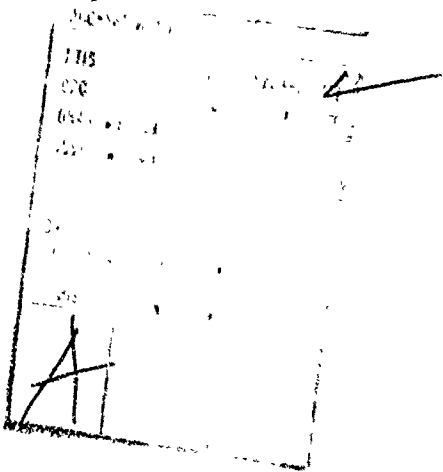
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iii

This concludes a major part of our effort in studies of compounds of  $Gd^{+++}$  and  $Eu^{++}$  ions which are characterized by a spherical ground state. Investigations of exchange enhancement of La doped SmS reflects our developing interest in more complex rare earth systems.

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61

## SUMMARY

During the course of this program we have developed methods for growing single crystals of the very high melting rare earth chalcogenides. We have demonstrated that many of the binary compounds exist over a range of homogeneity (e.g. EuO, EuS, GdSe and  $Gd_{3-x}□_xS_4$ ) and that the resulting defect structures have profound effects on the physical properties of these materials. We have further shown that it is possible to grow single crystals of mixed valence compounds and obtain sufficiently large homogeneous regions for transport and magnetic measurements.

These materials represent an important subclass of magnetic semiconductors in which the moment of the 4f electrons is localized at each cation site. The interest in these materials derives primarily from the dramatic magnetic, optical and transport effects which are sensitive to changes in electron concentration. Among these are: 1) The insulator-metal transition (a 13 order magnitude effect) in EuO. This transition was shown to be magnetically driven and a microscopic model centered on the concept of the magnetic polaron was developed; 2) Tunneling properties of EuS. The temperature dependence of the tunneling conductance was explained on the basis of critical scattering of electrons by magnetic fluctuations and conduction band splitting below the ordering temperature. These concepts were verified experimentally; 3) Anomalous transport properties of EuS and  $Gd_{3-x}□_xS_4$ . It was demonstrated that the band tail model for disordered materials, modified to include magnetic interactions, successfully describes the experimental results; 4) Color changes in the

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This concludes a major part of our effort in studies of compounds of Gd<sup>+++</sup> and Eu<sup>++</sup> ions which are characterized by a spherical ground state. Investigations of exchange enhancement of La doped SmS reflects our developing interest in more complex rare earth systems.

## TABLE OF CONTENTS

	PAGE
I. INTRODUCTION	1
II. MATERIALS	2
III. PHYSICAL MEASUREMENTS	6
IV. CONCLUSION	11

## I. INTRODUCTION

This report summarizes a three year effort in the study of the synthesis of rare earth compounds and an investigation of their magnetic, optical and semiconducting properties.

We shall trace the development of the growth of single crystals from the simple face centered cubic magnetic insulating rare earth chalcogenides, to the more complex  $\text{Th}_3\text{P}_4$  type structures and lower symmetry layer compounds. Our objectives include the synthesis of higher purity materials, the improvement of crystal perfection, and measurement of deviations from stoichiometry. We develop the techniques for growing single crystals of varying compositions of solid solutions between di and trivalent rare earth chalcogenides and methods used for their characterization.

In addition we will develop the reasoning which led to the variety of experiments referred to in the body of this report, with emphasis on the relationship between magnetic and electronic properties of these systems. We probe the direct relationship of magnetism to the band structure as reflected in transport, tunneling and optical measurements.

## II. MATERIALS

In this, the final report of three years of research under ARPA Contract DAAH01-70-C-1309 and DAAH01-71-C-1313, we present the results of our work and refer only to publications which were generated by this support. Since we have published continuously during the term of the contract, the references cited will take the reader to the open literature.

At the initiation of the contract, in June 1970, we had established that single crystals of the europium chalcogenides could be grown, that they were magnetic semiconductors, and that it was possible to significantly increase the Curie temperatures of these compounds by doping with trivalent rare earths. Our original interest had been an exploration of the very dramatic changes in magnetization with changes in electron concentration.

Some work had been done on the transport properties of these materials and this revealed very large effects of magnetic ordering on the semiconducting properties of the compounds. With growing interest in these semiconducting properties it became clear that refinement of crystal growing techniques, with emphasis on reproducibility, improved purity and perfection, was of the utmost importance.

Our first task was to develop a system which would repeatedly reach the very high temperatures ( $\sim 2500^{\circ}\text{C}$ ) required for crystal growth. Two systems evolved, one using a tungsten mesh resistance furnace<sup>(1)</sup> and the second a vacuum rf furnace with direct coupling to the crucible.<sup>(2)</sup> Both systems were found to give excellent temperature control and have been used to produce all the materials studied in the course of this program.

The next phase of the program involved the synthesis of higher purity materials and a means of controlling crystal stoichiometry. Since the purity of rare earth metals and oxides has steadily improved over the years, no effort was made to further refine the suppliers' metals. We did, however, find that the method of shipment commonly used permitted deterioration of metals in transit. Protective oils or sealing waxes used in packaging were found to contribute to serious contamination. We have therefore required that all metals be shipped in sealed quartz containers filled with purified inert gas. The metals no longer arrive discolored by surface oxidation. The purity of recently received europium metal is approximately 99.99% and that of the oxide about 99.999%.

During efforts to grow and characterize single crystals of EuO and EuS it became evident that these 'compounds' existed over a range of homogeneity with solid solubility almost entirely on the metal rich side of the stoichiometric compound. Non-stoichiometric crystals are "n" type with vacancies on anion sites. The development of crystal growing methods which permitted control of vacancy concentration was correlated with the development of methods for characterizing single crystal samples.<sup>(3,4)</sup>

Synthesis of the sulfide from  $\text{Eu}_2\text{O}_3$  with  $\text{H}_2\text{S}$  was investigated at very high temperatures in order to determine the optimum temperature for production of EuS with minimal oxygen contamination.<sup>(5)</sup> The growth of single crystals of EuS with variation in excess Eu metal concentration established that a nonhomogeneity range existed for this compound.<sup>(6)</sup>

Deviation from stoichiometric compound formation was also studied for trivalent rare earth metallic compounds. Previous reports indicated that

solid solubility occurred only in the metal rich region of these systems. Such limited homogeneity was found for GdS, but GdSe showed an extraordinarily large homogeneity range extending to about 7 % into the anion field. Single crystals of the selenide exhibited the normal gold metallic color for the stoichiometric composition but the color changed progressively toward the blue with increasing cation deficiency.

With the initial success in treating transport in disordered EuS<sup>(6,7)</sup> we directed our attention toward the  $\text{Th}_3\text{P}_4$  type magnetic semiconductor systems. Representing the rare earth compounds by  $\text{RE}_{3-x}^v\text{X}_4$  (where  $x = \text{S, Se, Te}$ ;  $v = \text{vacancy}$  and  $0 \leq x \leq 1/3$ ) it was found that these materials change continuously from metals to insulators with increasing vacancy concentration,  $x$ , with the insulator being antiferromagnetic and the metal ferromagnetic. Although crystals of various compositions of the  $\text{Gd}_{3-x}^v\text{S}_4$  and  $\text{Gd}_{3-x}^v\text{Se}_4$  have been grown successfully with different vacancy concentration,  $x$ , we still have difficulty measuring composition with standard analytical techniques. Systematic transport and magnetic measurements have thus far been relied upon for sample characterization.<sup>(9,10)</sup>

Investigations of pseudobinary solid solution systems, in order to study effects of different dopants on magnetic and electrical properties, were further explored. The substitution of monovalent anions for the divalent chalcogenide was found to increase magnetic ordering temperatures.<sup>(11)</sup> In the limited range of solubility of these systems essentially the same increase in paramagnetic Curie temperature was observed as that for the substitution of trivalent cations for europium.

Experiments with the formation of solid solutions between Eu chalcogenides and trivalent rare earth chalcogenides using sintering techniques

were only marginally successful because of the difficulty in producing homogeneous samples by this technique. We therefore decided to grow crystals from the melt, knowing that concentration gradients developed during growth. The sampling techniques then became critical, but we found that if small sections were cleaved from the crystals, electron microprobe analysis could be used to select sufficiently large homogeneous regions for physical measurements. All transport, magnetic, optical and x-ray measurements were then made on the same crystal section. This technique was used in the study of the pseudobinary europium-gadolinium sulfide system and the  $\text{Sm}_{1-x}\text{La}_x\text{S}$ . (12,13,14,15)

All materials investigated thus far had relatively simple cubic structures lacking crystalline anisotropy. A considerable interest had been developing in the transition metal layer dichalcogenides. These compounds have single layers consisting of metal ions strongly bonded between two sheets of chalcogenides. Adjacent layers are weakly bonded to each other making it possible to introduce other ions or molecules in the gap between layers without disturbing the atomic arrangement (intercalation) within a given layer. Normal high temperature reactions with alkaline earth or rare earth ions generally yield three dimensional structures. The divalent rare earths Eu and Yb, which are soluble in liquid ammonia, have been intercalated in the group IV, V and VI dichalcogenides at low temperatures. Ferromagnetic order is seen in the Eu intercalated compounds for concentrations greater than  $\text{MS}_2(\text{Eu})_{0.5-0.6}$ . The Yb intercalated compound  $\text{MoS}_2(\text{Yb})_x$  becomes superconducting at 2.4°K. (16)

This materials program has taken us from the simple cubic



ferromagnetic semiconductors through disordered magnetic materials to the highly anisotropic layer dichalcogenides. Intimately woven into the development of this program are the physical measurements described in Section III.

### III. PHYSICAL MEASUREMENTS

Our research effort in studying the various physical properties of rare earth chalcogenides, particularly those containing Eu, stems fundamentally from the observation that the magnetic behavior of these compounds is an extremely strong function of the electron concentration. It was clear that the conduction electrons altered the exchange interaction in a systematic way and that the conduction electron localized 4f spin exchange interaction played a dominant role in this.

An obvious hypothesis to test was, therefore, the following: given that conduction electron-localized spin exchange accounts for the magnetic behavior, is there a concomitant strong dependence of electronic motion on the magnetic state of the system?

To answer this latter question we have, in addition to the standard tools (i.e., resistance, magnetoresistance, Hall effect and thermoelectric power) used photoconductivity and tunneling methods to describe transport in magnetic semiconductors. Furthermore, we have developed techniques to perform experiments on small single crystal samples of these refractory materials (on the order of  $3 \times 3 \times 10$  mils) and have prepared new alloys, such as LaAg eutectic, to form ohmic contacts.

Transport measurements in EuSe and EuS had already established the anomalous giant negative magneto-resistance effect and critical electron

scattering by magnetic fluctuations. But there still remained, at least in the lightly doped, semiconducting samples, the unanswered question as to whether or not the magnetoresistance effects are due to changes in mobility or changes in free carrier density. Resistivity measurements alone cannot answer this question since the conductivity is a carrier density mobility product,  $\sigma = ne\mu$ . Hall effect measurements, at the magnetic field strengths available to us, could not be effected because the magnetoresistance effects swamped any Hall signal. The photoconductivity experiments<sup>(17)</sup> were undertaken to answer this question in EuSe, the most thoroughly studied material at that time.

The d.c. photoconductivity measures the quantum efficiency - mobility - lifetime product,  $\beta\mu\tau$ . Transient photoconductivity measurements, on the other hand, measure  $\beta\mu$  and the decay time,  $\tau'$ , separately if the photoexcitation occurs in a time small compared to  $\tau$ . The work of Penney and Kasuya<sup>(17)</sup> demonstrates, by comparing transient and d.c. photoconductivity experiments with resistivity measurements in doped EuSe samples, that the mobility dominates the variation in the conductivity.

Our continuing interest in transport properties was heightened by the discovery at MIT that certain samples of EuO undergo an insulator-metal phase transition near the magnetic ordering temperature ( $T_c \sim 69^\circ\text{K}$ ). Penney, et al<sup>(18)</sup>, were able to demonstrate a direct relationship between the conductivity activation energy and the magnetization. This result was observed in Eu rich samples, in which the resistivity changes by more than 13 orders of magnitude and showed that the transition is magnetically driven.

Such clear-cut evidence for the mechanism for phase transitions is unusual and has stimulated further research in several laboratories.

The fact that the magnitude and temperature variation of the resistivity was observed to be strongly dependent on sample preparation led to a thorough study of the relationship of crystal growth parameters to the stoichiometry of  $\text{EuO}$ .<sup>(3,4)</sup> The latter was determined by correlating the infrared absorption, conductivity and microstructure with the  $\text{Eu/O}$  ratio of the starting compositions. These studies determined a new phase diagram for  $\text{EuO}$  which has since been used as a guide for growing  $\text{EuO}$  crystals of well defined composition.

The above-mentioned experiments involved defect structures (in contrast to the doping with trivalent rare earths) in which the extra electrons are trapped near the oxygen vacancy sites. This prompted a re-examination of the electronic ground state of singly and doubly occupied vacancies and ultimately led to a new description of the magnetically driven insulator-metal transition in terms of a bound magnetic polaron. This model differs from earlier models in that it assumes that the two electrons do not occupy the same orbit. Thus we can envision a ground state for the electrons exhibiting a finite moment which can couple to the localized  $4f$  spins. The name "bound magnetic polaron" derives from the idea that the electrons are localized both by the magnetic interaction and by the coulomb field of the vacancy. Torrance and co-workers<sup>(19,20)</sup> were able to explain consistently both infrared and high temperature (above  $T_c$ ) magnetic data using this model. The latter data, which showed that the high temperature susceptibility and extrapolated Curie

temperature were dependent on the oxygen vacancy concentration, would not have been predicted by earlier models.

During this period we also decided to make a concentrated effort to study the magneto-transport properties of the EuS. Previous experience had demonstrated that Schottky-barrier tunnel junctions could be fabricated with In on appropriately doped EuS. Inelastic scattering effects in the barrier, modulated by magnons, had been examined. Elastic scattering, on the other hand, had not been studied in detail. Furthermore EuS was observed to be chemically the most stable of the Eu chalcogenides and the only one in the group, other than EuO, which was a true ferromagnet. It was also thought that the low Curie temperature (16°K) would enhance changes in physical properties with applied magnetic field (the lower  $T_c$ , the smaller the energy necessary to change the magnetic order of the system). As in the EuO case, the carrier concentration was found to vary with stoichiometry. In the process of perfecting techniques for controlling the vacancy concentration to produce samples satisfactory for tunneling studies, a series of excellent EuS samples spanning the concentration range from insulator to metal were generated.

Tunneling studies were carried out on two classes of samples: 1) those having electron concentrations less than  $5 \times 10^{18} \text{ cm}^{-3}$ , which were used as capacitance probes and 2) those having more than  $\sim 10^{19}$  carriers, which were used in the tunneling studies. Capacitance measurements on the lower concentration samples gave the barrier height of the Schottky barrier, its change with magnetic order, and thus the absolute value of the conduction band shift.<sup>(6)</sup> To the best of our knowledge this experiment

represents the first "direct measure" of conduction band splitting in the presence of a (internal) magnetic field. The higher concentration samples exhibited an anomaly in the tunneling conductance near  $T_c$  and this was explained in terms of electron critical scattering in the barrier. The predicted magnetic field dependence of the conductance was also observed. In addition, well characterized samples made possible a systematic study of electron transport in  $\text{EuS}$ <sup>(7)</sup>. This led to an explanation for electronic motion in terms of a band tail model with disorder produced by the vacancies. One particular success of the model was its ability to predict the low temperature resistivity behavior, in the hopping regime, from the high temperature data.

It is remarkable that the assumption of a band tail works as well as it does. The samples were chosen by varying the Eu/S ratio and one might expect the density of electron states to change substantially as a function of concentration. Apparently there is some contribution of unknown defects common to all samples.

These observations led us to test accepted models of transport in band tails by choosing materials where a rigid band is expected to apply. The  $\text{Th}_3\text{P}_4$  system lends itself particularly well to such studies, since the structure can accommodate a large number of vacancies randomly distributed throughout the lattice at the Th sites. These sites can be partially filled to provide carriers, but as long as the ratio of vacancies to conduction electrons is small, a rigid band model ought to be valid. We have studied the transport properties of single crystals of the magnetic semiconductor  $\text{Gd}_{3-x}\text{V}_x\text{S}_4$ , where  $v$  denotes vacancies<sup>(9,10)</sup>. We were able

to interpret the results of resistivity, magneto resistance, and thermopower, in terms of a band tail model, but extended to include magnetic interactions.

Toward the termination of this program we began to investigate rare earth ions which do not have a spin only ground state. One interesting example is Sm, which, in its divalent state has no net moment ( $J=0$ ) but which develops "Van Vleck" paramagnetism. This paramagnetism arises because one or more excited state ( $J=1$ ) etc. is either thermally populated or admixed into the ground state by the externally applied magnetic field. The relevant parameter is the energy difference between the  $J=0$  and  $J=1$  states which, in Sm chalcogenides, is modified by an indirect exchange between the  $\text{Sm}^{2+}$  ions, via the conduction band. In order to explore this enhancement we have studied the solid solution system  $\text{Sm}_{1-x}\text{La}_x\text{S}$ . The effects of the extra electron contributed by the La ion reach a maximum near 3% La concentration as exhibited in the enhancement of the Van Vleck susceptibility.<sup>(14,15)</sup> We hope to continue investigation into the effects of other dopants on  $\text{Sm}^{2+}$ - $\text{Sm}^{2+}$  exchange interactions.

#### IV CONCLUSION

During the course of this program we have developed methods for growing single crystals of the very high melting rare earth chalcogenides. We have demonstrated that many of the binary compounds exist over a range of homogeneity (e.g.  $\text{EuO}$ ,  $\text{EuS}$ ,  $\text{GdSe}$  and  $\text{Gd}_{3-x}\text{S}_4$ ) and that the resulting defect structures have profound effects on the physical properties of these materials. We have further shown that it is possible to grow single crystals of mixed valence compounds and obtain sufficiently large homogeneous

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