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Halide Doping of Ferromagnetic Europium Chalcogenides

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The europium chalcogenides EuO, EuS, and EuSe are insulating ferromagnets at low temperatures. Rather large increases in their Curie temperature can be effected by doping to increase their electrical resistivity. Previously the doping species have been cation substitutions of "trivalent" rare earth ions or Eu-metal. It is shown here that the monovalent halide ions, particularly Cl^-, are very effective in increasing the conductivity and Curie temperature of EuS and EuSe.

The increases in electrical conductivity, and the sharpness of the magnetic transition temperatures, as determined by initial permeability measurements, are strongly related to the doping concentration. Between about 1 and 1.5% chloride doping in EuS, the magnetic inhomogeneity at the transition temperature is sharply lowered and the conductivity shows a marked increase. The different environments of the dopant, whether it is on the anion or cation site, and their effect on the spin cluster formation are discussed.

Introduction

Pure, undoped europium chalcogenides, EuO, EuS, and EuSe, are insulating ferromagnets at low temperatures, but rather large increases in their Curie temperatures can be effected by doping to increase their electrical resistivity (*1–4*). A considerable amount of work has been done in the past to elucidate this relationship between the magnetism and the conductivity which results from the addition of impurities, i.e., dopants, to the chalcogenide (*2*, *3*, *4–7*). In previous studies the doping species were mainly cations such as the "trivalent" rare earths, which form solid solutions of the EuS-RES type, or Eu-metal. Despite the fact that halide ions are commonly used in the doping of the more conventional semiconductors, there has been only preliminary work published (*8*, *9*) to show what effect such substitutions may have on the ferromagnetic europium chalcogenides. This paper reports on such a study and shows that the monovalent halide ions, particularly Cl^-, are very effective in increasing the conductivity and the transition temperature of EuS and EuSe.

Experimental

The europium sulfide was prepared by the reaction of high purity H_2S gas and 99.99% pure Eu_2O_3 at 1100°C. The oxygen content of the resulting EuS, which was used as the starting material, was less than 100 ppm (*10*). The EuSe was prepared by F. Holtzberg by direct reaction of the elements. The europium halides were also obtained from the oxide by first dissolving in the appropriate mineral acid, evaporating to dryness, and then heating to above the melting point in the appropriate hydrogen halide atmosphere. Millimeter-sized crystals, which were oxygen- and water-free, were obtained by this method. Since the divalent europium halides are hydroscopic, all subsequent handling was done in a dry box.

The doping, i.e., the reaction between the halide and the chalcogenide, was accomplished by sealing the intimately mixed desired compositions in tungsten crucibles. The sealing was done in vacuum by electron beam welding. The crucible was then rf heated to above the liquidus temperature of the mixture. Since the liquidus temperatures of these mixtures were not known very precisely, the temperature from which they were cooled was in all

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cases that of the approximate melting point of the pure chalcogenide, i.e., 2500°, 2320° for EuS and EuSe, respectively. The cooling rates were roughly 5–8°/hr for the first 200° and roughly 400°/hr between 2000° and room temperature. From melts cooled in this manner, single crystals large enough to evaluate, and on which the physical measurements were made, could easily be separated. In some runs, crystals as large as 8–10 mm were obtained.

The single crystals, and in many cases the surrounding matrix, were analyzed by the electron microprobe for halide, europium, and sulfur. The Curie temperatures (T_c) were measured by an initial permeability method where a small external ac field is applied and at the Curie point, where the permeability (μ) is infinite, a sharp break in the u vs. T curve is observed. The magnetization and paramagnetic Curie temperatures θ were obtained with a force-type magnetometer from 4.2 to 300°K. The resistivity measurements were made by a two-probe technique using indium contacts.

Results and Discussion

Although all three chalcogenides, EuS, EuSe, and EuTe, could be doped with halide, the sulfide was examined in the most detail and the following discussion will be primarily concerned with it. The compositions studied in the sulfide system are shown by the closed circles in Fig. 1. This shows the EuS-rich portion of the ternary system EuS–$EuCl_2$–Eu. It should be noted that most of the compositions studied lie on the join between EuS and the hypothetical compound EuCl. In other words, equal quantities of $EuCl_2$ and Eu-metal were reacted with the EuS to produce these starting compositions. Compositions along the EuS-$EuCl_2$ join, those with no Eu-metal added, were shown to have essentially the same properties as the pure EuS even though chloride was present in the lattice. It is assumed that these compositions contained only Eu vacancies, probably close to the singly negatively charged Cl^-. As Eu-metal is added to a given EuS–$EuCl_2$ composition it apparently fills the vacancies and along the EuS–"EuCl" join it is assumed they are all filled. Further increases in the Eu-metal concentration will then just result in the formation of sulfur vacancies which act as donors similar to the trivalent rare earth ions. The transport properties of such compositions have been previously discussed (*11*, *12*) and will not be considered here.

The relationship between the final chloride concentration found in the crystals and that added as $EuCl_2$ along the EuS–EuCl join is shown in Fig. 2. It should be pointed out that this is an unusual relationship which may initially appear to be a violation of the phase rule because the chloride solubility at a given temperature is a function of its concentration! An explanation for this behavior is that the solubility is also determined by the partial pressure of chlorine over the melt, which is contained in a closed system. It is presumed that this pressure, which results from the dissociation of $EuCl_2$, increases with concentration. In any case, a maximum solubility of about 1.5 mol% Cl^- is obtained from an initial concentration of 12–14% $EuCl_2$. The excess was found as fine-grained material uniformly distributed in the grain-boundaries, which presumably prevented the growth of large crystals. Analyses of crystals taken from various regions of

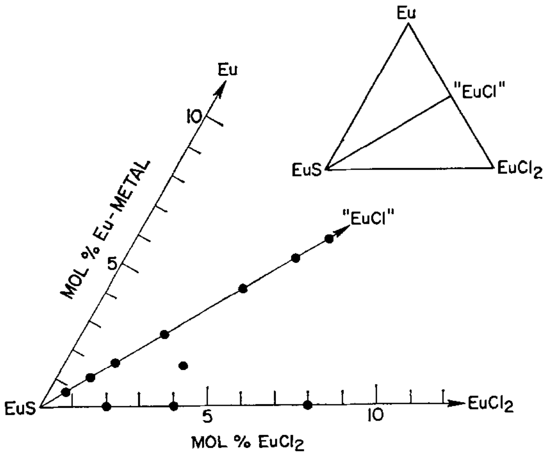

FIG. 1. Compositions studied (closed circles) in the ternary system EuS–$EuCl_2$–Eu.

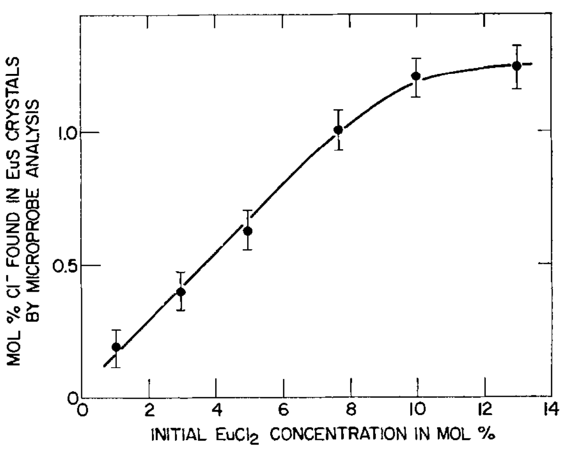

FIG. 2. Relationship between starting $EuCl_2$ concentration and that found in the final crystal.

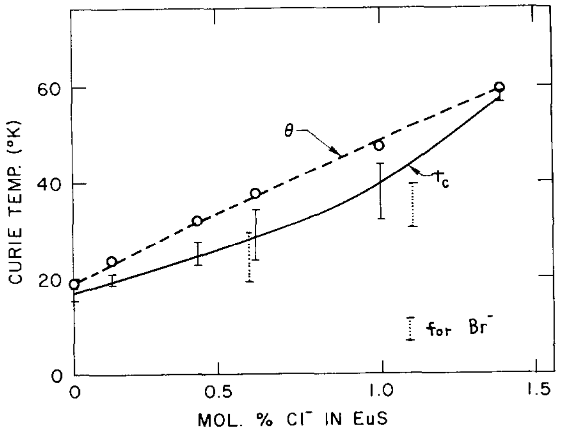

FIG. 3. Curie temperature variations with chloride concentration in EuS crystals. Dashed curve is paramagnetic Curie temperature θ, and solid curve the ferromagnetic Curie temperature T_c (see text).

the crucible did not show any gross compositional differences and back reflection X-ray measurements did not show any significant lattice constant differences between the chloride-containing and the pure material.

The magnetic data are presented in Figs. 3 and 4. In Fig. 3 the paramagnetic (θ) and ferromagnetic (T_c) Curie temperatures are shown as a function of chloride concentration. It is seen that both T_c and θ show sharp rather linear increases over the doping range studied. This increase of roughly 40°K for EuS is the largest which has been reported to date.

The linear increase of θ and T_c with chloride concentration is consistent with the model of Kasuya and Yanase (*7*) which predicts $\Delta\theta$ to be proportional to the doping level in the 0–5 % range and to ΔT_c in the 0–1 % range. In their theory, the dominant Eu–Eu(f–f) exchange interaction is indirect through *s* or *d* electrons. Therefore, the addition of donors should increase the overall exchange interaction.

The θ's obtained from the high temperature susceptibility are in all cases higher than the T_c's. This is normally what is seen in compounds such as these and has been discussed in terms of the cluster model of Kasuya and Yanase (*7*). In this model, a cluster of ordered spins forms on the nearest and next-nearest neighbors of the impurity atom because of the enhancement of the exchange interactions by electrons contributed by the impurity. The difference $(\Delta\theta - \Delta T_c)$ is explained by an antiferromagnetic exchange interaction between the clusters, I_{eff}. Since this is a parameter which is adjustable and which we have no independent method of determining, the differences shown should not be considered significant in terms of the model, nor should they be used to evaluate I_{eff}. It is found that the transitions obtained from the initial permeability measurements are not as sharp for the intermediate concentrations (see Fig. 4). The vertical bars on the T_c curve of Fig. 3 do not show the error in determining the Curie temperature by this method, but rather show the temperature range over which ordering occurs. It may be expected, however, that at the highest chloride concentrations, where the giant clusters are likely to overlap, a more uniform magnetic state is

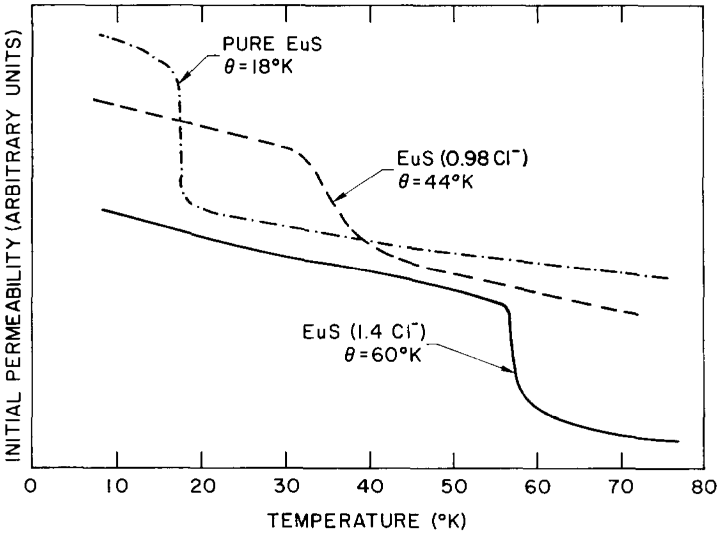

FIG. 4. Selected curves showing the variation of the initial permeability with temperature.

produced and θ-T_c differences more consistent with the undoped material would be observed.

Figure 4 shows the changes in the initial permeability at the ordering temperatures for three samples of differing chloride concentrations. The three samples represent three doping levels, i.e., the zero or very lightly doped case shown by the dashed-dot line, the intermediately doped case by the dashed line, and the heavily doped one by the solid line. It should be noted that sharp transitions are seen for both the pure EuS and the heavily doped material. This undoubtedly reflects the existence of considerable magnetic inhomogeneity in the region of the transition temperature in the intermediately doped samples. From an examination of the initial permeability curves, it can be concluded that this inhomogeneity is sharply reduced at a composition containing 1–1.4% chloride. Evidence of magnetic inhomogeneity is also obtained from the magnetization measurements which, for the medium doped samples, show a "tail" in the σ vs. temperature curve in the vicinity of the Curie point.

Resistivity measurements strongly indicate that a change in the transport mechanism also occurs between the 1 and 1.4% chloride samples—the same point where the permeability measurements indicate a more homogeneous magnetic state. This apparent change is based on the magnitude of the characteristic anomalous peak (*2*) in the resistance near the Curie point. For the low and intermediate concentrations, large well-defined resistivity peaks are observed which are slightly broadened at the 1% level. However, at the highest concentration (1.4%) only a broad bump, several orders of magnitude smaller, is seen. This behavior is consistent with the previous observations of rare earth doped chalcogenides in that the size of the anomalous peak and the transport mechanism are strongly dependent on the impurity concentration (*2*, *5*, *13*). At low concentrations, conduction is presumed to be thermally activated hopping between localized impurity states, while at the higher doping levels an impurity band-like model is used to describe the transport, with the small peak at T_c being a result of critical scattering. The site occupied by the chloride ion has a lower electron affinity than the other equivalent anion sites and acts as a donor lying just below the conduction band just like the "trivalent" rare earth ions.

The results of both the permeability and resistivity measurements can also be interpreted in terms of the cluster model. These measurements showed there is a critical concentration of about 1.0–1.4% chloride at which the magnetic inhomogeneity is sharply reduced and the conductivity presumably changes from hopping to band-like. It can be argued that this is the concentration where the clusters of oriented spins begin to overlap and where the difference between the exchange interactions within the clusters and those in the matrix is small. In fact, the agreement between the observed concentration where the conduction process changes from hopping to band-like and that predicted by the simple theory (*5*, *7*, *16*) is good, i.e., roughly 1%.

Using the critical concentration, and assuming an ideal lattice where all the chlorides are distributed homogeneously, one can obtain a rough estimate of the effective cluster size. This yields a cluster containing about eighty Eu^{2+} atoms which are located within a radius of slightly beyond the third coordination sphere of the chloride. This is in rough agreement, if not a bit larger, than a cluster which includes only nearest and next nearest neighbors, as predicted for the cation doped materials (*14*, *15*). It is not unreasonable to expect a different effective cluster size between the cation and anion doped materials because there is a distinct difference in the europium environments between the two. In the cation doped material, the dopant occupies a Eu site which has twelve nearest and six next-nearest neighbors. On the other hand, when a dopant such as chloride occupies a sulfur site its immediate environment is six Eu-atoms in an octahedral configuration, and in the second coordination sphere there are eight Eu's in a cubic configuration. There are no intervening anions between the dopant and any europium ions until the third coordination sphere is reached. Thus, the number of Eu-atoms which see the dopant directly is significantly higher, and they are at closer distances than in the case where the dopant is on the Eu-site. As a result of this, it is likely that the distribution and degree of overlap of the europium wave function will be significantly different, particularly those in the first and second coordination sphere. Consequently, the impurity wave functions which form the spin clusters will be altered.

Finally, in the cluster size estimation, as well as the other magnetic measurements, the measured chloride concentration was assumed to be the actual impurity concentration which contributed electrons. In reality, we know this is not entirely true since mass spectrographic analyses showed a foreign ion impurity level of 800–1200 ppm. Further, and probably more important will be the degree of compensation or "overcompensation" of the chloride by the Eu-metal. In this case, where there is an excess of Eu-metal, the composition will fall above

TABLE I

Starting composition			Final halide content (mol%)	Curie temperature (°K)
EuS	Eu	EuBr$_2$		
96	2	2	0.52	28°
84	8	8	1.10	39°
EuSe	Eu	EuCl$_2$		
96	2	2	—	18°
90	5	5	0.85	—
EuSe	Eu	EuBr$_2$		
94	3	3	0.48	12°–15°

the Europium side of EuS–"EuCl" join in Fig. 1. Thus, the excess Eu-metal will also act as a dopant by creating sulfur vacancies and the true doping level will be higher than that measured.

As was previously stated, other europium chalcogenides were doped with halide ions but were not investigated in detail. Table I briefly summarizes the results of these experiments.

It is seen that very similar increases in the Curie temperature are found in bromide-doped EuS and that EuSe can be doped by both chloride and bromide.

Conclusions

It has been shown that the monovalent halide ions, Cl and Br, can be substituted into the ferromagnetic europium chalcogenides and are extremely effective in changing their transport properties and increasing their Curie temperature. For example, 1.4 mol% Cl substitution in EuS causes a $3\frac{1}{2}$ times increase in T_c. At a doping level of 1.0–1.4 mol% chloride in EuS, the conductivity appears to change from nonmetallic to metallic-like and the transition temperatures as measured by the initial permeability become much sharper. It is assumed that at this critical concentration the clusters of oriented spins around the chloride ions begin to interact with each other. A cluster size which extends to slightly beyond the third coordination sphere and includes about 80 Eu atoms is estimated from this critical concentration. For the halide-doped materials, there are more nearest and next-nearest neighbor europiums closer to the dopant and not separated from it by other chalcogenide ions; so any differences between the halide- and cation-doped materials are perhaps a result of this.

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