# NEUTRON DIFFRACTION STUDY OF MAGNETIC ORDER IN THE TERNARY SUPERCONDUCTOR $ErMo_6Se_8$

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## ABSTRACT

Development of new ternary superconductors has led to materials which also show a strong tendency toward magnetic order when one of the constituent elements is a rare earth. Powder neutron diffraction data on superconducting ($T_s \sim 6$ K) samples of $ErMo_6Se_8$ taken in the temperature range 0.05-2.0 K show that magnetic Bragg peaks develop at $T_M = 1.1$ K, in agreement with specific heat studies. However, it is not possible to index these new reflections using a simple antiferromagnetic unit cell based on the $ErMo_6Se_8$ lattice. It is also not possible to index the magnetic reflections based on a single modulation vector, or with a modulation vector along a high symmetry direction including higher order harmonics. Thus either the long range magnetic order corresponds to a more complicated magnetic structure in the $ErMo_6Se_8$ lattice, or at least some of the peaks develop in impurity phases. These results are compared with the recent neutron data on the reentrant superconductors $HoMo_6S_8$ and $ErRh_4B_4$, in which the development of ferromagnetic order is clearly shown to be responsible for quenching the superconductivity.

## INTRODUCTION

The ternary molybdenum chalcogenides belong to a new class of superconducting materials which display a variety of interesting and unusual properties. They have modestly high superconducting transition temperatures (up to $\sim 16$ K), yet possess very high upper critical fields (up to 700 kOe).[1] Moreover, the materials which contain rare earth elements are not only superconducting, but exhibit a strong tendency toward magnetic order as well.[2] Initially we have chosen to study $ErMo_6Se_8$, which has a superconducting transition temperature of 6 K. Measurements of the specific heat and d.c. susceptibility demonstrate that there is another phase transition at 1.1 K,[3] with the material remaining superconducting. If this lower temperature phase transition does indeed correspond to a state with long range magnetic order, then these materials would be the first examples of the simultaneous coexistence of these two cooperative phenomena. This behavior contrasts with that of $HoMo_6S_8$[4] and $ErRh_4B_4$[5] recently reported, where the magnetic ordering destroys the superconductivity.

The neutron scattering technique is ideally suited to study these types of materials since the magnetic phenomena can be probed directly without being influenced by the screening effects of the superconducting electrons. Furthermore, the neutron is particularly sensitive to the magnetic ordering of the Er ion because its magnetic cross-section is an order of magnitude larger than a typical nuclear cross-section. The preparation of the powder samples, which are the same samples used by McCallum, et al.,[3] has been described elsewhere.[6] The measurements were taken with a triple-axis spectrometer at the High Flux Beam Reactor at Brookhaven. The incident wavelength was $\lambda = 2.463$ Å, with a pyrolytic-graphite filter employed to suppress higher-order wavelengths. The sample was mounted in a helium dilution refrigerator which has a low temperature capability of $\sim 50$ mK. Ge resistance thermometers were used to measure the temperature.

## RESULTS AND DISCUSSION

Complete diffraction patterns over the range of scattering angles 1°→80° were measured on a sample with a nominal composition $Er_{1.2}Mo_6Se_8$. Data were taken at room temperature, 1.40 K (above the phase transition), 0.84 K and 0.07 K. In these data nuclear peaks in addition to those associated with the $ErMo_6Se_8$ Chevrel phase were observed, indicating the presence of secondary phases in the sample. The most prevalent phases were $MoSe_2$ and $Mo_3Se_4$. Since they are not magnetic, their presence should pose no problem in the present experiments, although it could be a problem with regard to the measurements of the superconducting properties. Other impurity phases which were identified in Ref. 3 were $Mo_5Si_3$ and $SiO_2$, none of which contain Er. However, our neutron and X-ray data, taken on the samples of Ref. 3, indicate that other impurities are present. Thus there is the possibility that relatively small amounts of Er-containing phases could be present and these might order magnetically at low temperatures.

By subtracting the data taken at 1.40 K from the data below the phase transition we can eliminate the scattering which is not associated with the phase transition and this difference pattern is shown in Fig. 1. The arrows indicate the positions of new peaks which are outside statistical error, the strongest magnetic peaks being clearly evident at scattering angles of 17.75°, 23.82°, 27.35° and 36.02°. In all cases the widths of the peaks were limited by our instrumental resolution. High resolution scans taken on the stronger peaks allowed us to place a lower limit on the magnetic correlation range of 190 Å. Thus these peaks correspond to long range magnetic order. We also note that there is a decrease in the intensity of the scattering away from the Bragg peaks below the phase transiition, which is expected due to the absence of paramagnetic scattering in the ordered phase.

Fig. 2 shows the temperature dependence of the magnetic peak at 27.35°. The magnetic phase transition occurs at $T_M = 1.05$ K, which agrees very well with the specific heat results.[3] The temperature dependence was also checked for the peaks at 17.75°, 23.82° and 36.02° with identical results. No change in the position of these peaks as a function of temperature was detected. For comparison the peak intensity of the {100} Chevrel nuclear peak is 8350 counts.

The crystal structure of $ErMo_6Se_8$ is rhombohedral ($R\bar{3}$), with one formula unit per unit cell. The Er ions occupy a simple primitive lattice, which is essentially cubic but with a small trigonal distortion. Since the rhombohedral angle is close ($\sim 1/2°$) to 90°, the splitting of the Bragg peaks away from cubic symmetry (for both nuclear and magnetic peaks) is small. Thus the description of the magnetic structure can be referred to a simple cubic Er lattice, but keeping in mind that there is a unique axis [111] in the system which may be important for determining the spin direction and domains.

Since none of the magnetic and nuclear peaks coincide, we can conclude that there is no ferromagnetic

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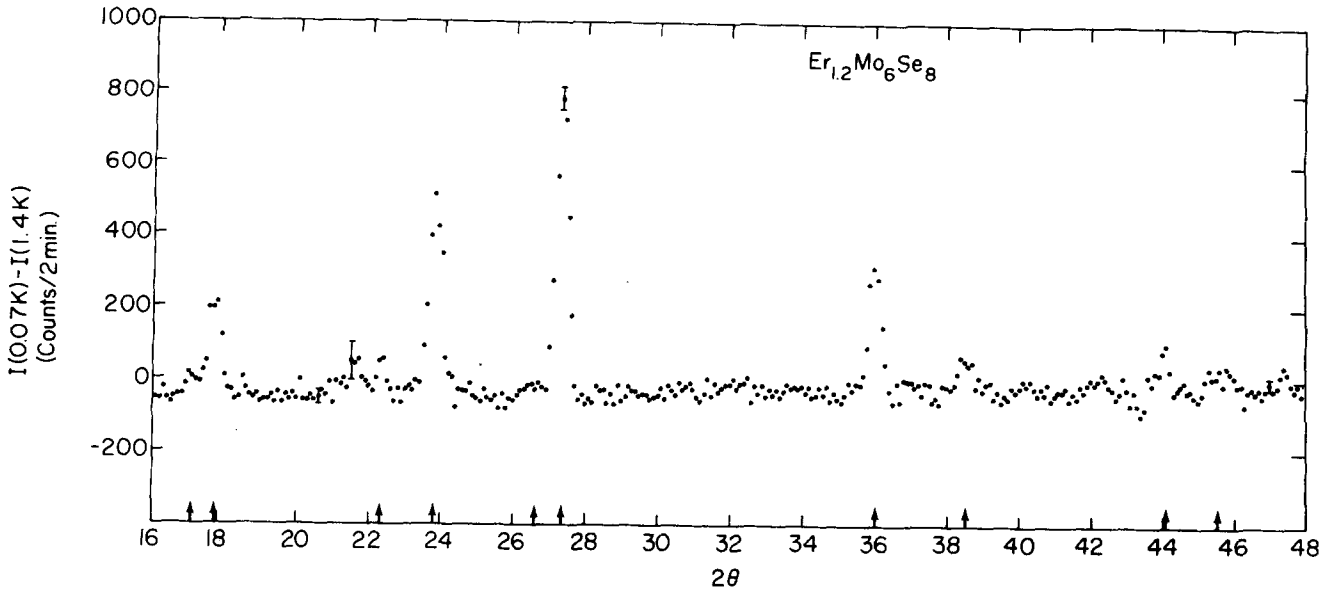


Fig. 1. Magnetic diffraction pattern for $Er_{1.2}Mo_6Se_8$. The data at 1.4 K (above $T_M$) have been subtracted from the data at 0.05 K. The arrows indicate the positions of new peaks which develop below $T_M$.

component in the structure. However, it is not possible to index the observed Bragg peaks on the basis of any simple antiferromagnetic unit cell. Since magnetic materials which involve rare earth constituents often exhibit more complicated modulated magnetic structures, we have tried to explain the positions of the observed peaks by modulating the basic magnetic lattice by a single plane wave. A modulation vector of $\delta$ = (0.23, 0.23, 0.23), for example, will produce the peaks at 17.75°, 23.82°, 27.35°, but will not explain the other peaks and predicts additional peaks which are not observed. Including higher order harmonics helps, but it is still not possible to explain all the observed peaks. We have found in fact that it is not possible to explain the positions of all the observed peaks on the basis of the Er lattice and a modulation vector of arbitrary magnitude and direction. This rules out, for example, the spin density wave structures, spiral structures, and any other modulated structure based on the type A, B, C or G structures.[8]

Thus the description of the magnetic structure must either be more complicated than can be described by a simple modulation vector, or at least some of the magnetic peaks belong to one or more impurity phases. In an attempt to clarify the situation measurements were taken on a second sample of nominal composition $Er_{1.0}Mo_6Se_8$. The second sample had considerably less impurity phases in it.[3] The powder diffraction data taken at 1.40 K were subtracted from the data at 0.05 K and are shown in Fig. 3. The data have been scaled with respect to the {100} nuclear peak intensity so that this data can be compared directly with the data in Fig. 1. The position of the {100} peak is also shown. We wish to make several points about the new data. First, the peaks at 17.75, 23.82 and 27.34° correspond to the same d spacings as found in sample 1, but the intensities of the peaks are a factor of three smaller. The temperature dependence of these reflections yielded a transition temperature of 1.10 K, in agreement with the results on sample 1. Since the impurity phases are less prevalent in this new sample, this would argue that the magnetic ordering is indeed associated with a secondary phase and not the Chevrel phase. However, additional magnetic peaks in the second sample are found at 21.6 and 30.5°, which are not observed in the first sample at all. Moreover, the transition temperature for these two peaks is 0.9 K. Careful examination of the specific heat measurements[3] also shows two peaks at 1.1 and 0.9 K, so the two sets of measurements agree that there are two phase transitions occurring in the second sample. In this regard we remark that two additional peaks at 10.6° and 13.85° were observed in the data of sample 1 at 0.07 K which were not present in the data at 0.84 K, and are not present at any temperature in the second sample.

It thus seems likely that at least some of the peaks which develop at low temperatures belong to one or more impurity phases. Since the ordering in the $ErMo_6Se_8$ lattice, if it exists, cannot be based on a

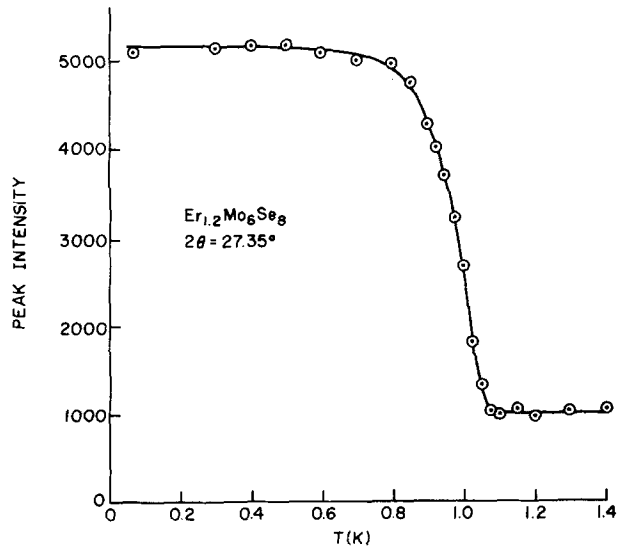


Fig. 2. The temperature dependence of the intensity of the Bragg peak at 27.35°, indicating a transition temperature of 1.05 K.

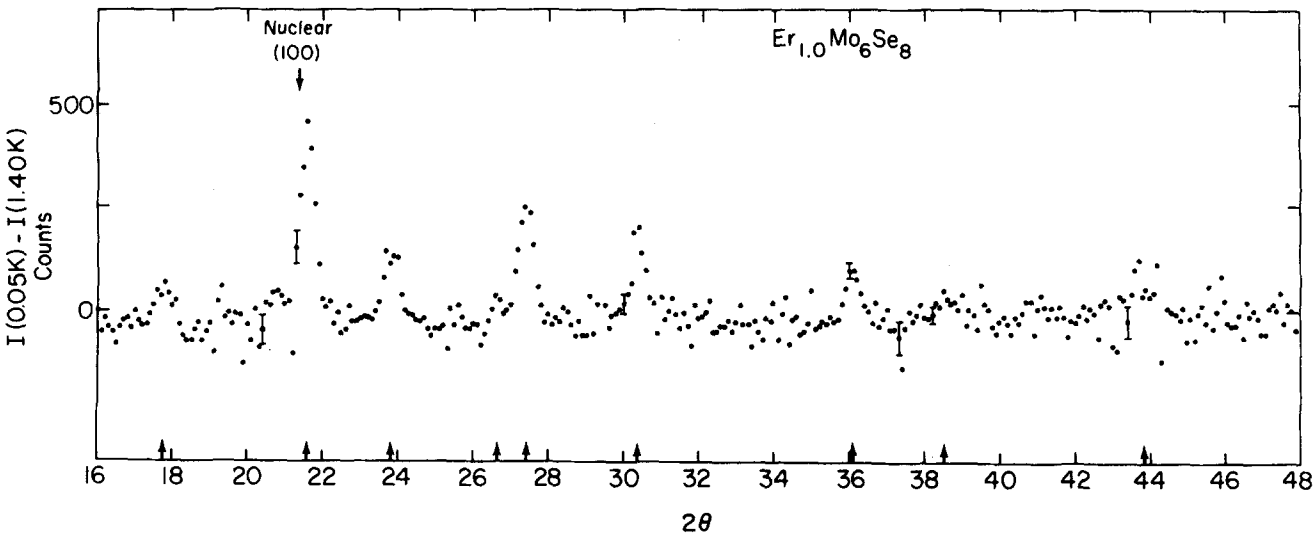


Fig. 3. Magnetic diffraction pattern for $Er_{1.0}Mo_6Se_8$. The intensity scale has been adjusted so that the intensity of the (100) nuclear peak is identical to that in the first sample (Fig. 1).

simple antiferromagnetic unit cell, it is very difficult to uniquely and reliably identify the type of magnetic ordering which is present. This contrasts with the situation in $HoMo_6S_8$ [4] and $ErRh_4B_4$,[5] where the magnetic ordering (which destroys the superconductivity) is ferromagnetic. In this case the positions of the magnetic peaks coincide with the nuclear peaks, providing an easy and unique identification between the chemical and magnetic unit cells. In such a case the presence of secondary phases is of little importance as far as the neutron scattering measurements are concerned. For $ErMo_6Se_8$ the observed magnetic and chemical unit cells are incommensurate, and so this easy identification does not exist. The excess entropy observed in the specific heat measurements[3] indicates that a substantial fraction of the Er ions participate in the magnetic ordering at $\sim$ 1 K, which tends to support the argument that the phase transition is occurring in the $ErMo_6Se_8$ and not in an impurity phase. It is likely that the details of the magnetic ordering will not be unambiguously determined until an impurity free sample is available. Further work is in progress.

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