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J. Budnick, K. Raj, T. Burch, F. Holtzberg. A NUCLEAR MAGNETIC RESONANCE STUDY OF THE MAGNETIC STRUCTURE OF EuSe AND ITS DEPENDENCE ON GADOLINIUM ADDITIONS. *Journal de Physique Colloques*, 1971, 32 (C1), pp.C1-763-C1-765. 10.1051/jphyscol:19711266 . jpa-00214097

**HAL Id: jpa-00214097**

**<https://hal.science/jpa-00214097>**

Submitted on 4 Feb 2008

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## A NUCLEAR MAGNETIC RESONANCE STUDY OF THE MAGNETIC STRUCTURE OF EuSe AND ITS DEPENDENCE ON GADOLINIUM ADDITIONS

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**Résumé.** — La résonance magnétique nucléaire des noyaux Eu et Se a été observée sous la forme pulvérisée de EuSe et EuSe contenant approximativement 1 % et 10 % de GdSe respectivement. Différentes structures magnétiques sont obtenues à partir des valeurs de résonance de Eu en fonction du champ et de Se en fonction du champ et de la température. Les résultats obtenus avec des échantillons de Gd dopés confirment l'existence d'une grande contribution négative aux champs hyperfins de Se et Eu tels que suggérés par les expériences d'aimantation macroscopique mais qui jusqu'à présent n'avait pas été observée dans les études microscopiques de ce système. On observe des changements considérables dans la relaxation du système de spins quand les champs magnétiques augmentent.

**Abstract.** — The nuclear magnetic resonance of both Eu and Se nuclei have been observed in powdered EuSe and EuSe containing approximately 1 % and 10 % GdSe. From the field dependence of the Eu resonance and the temperature and field dependence of the Se resonance we obtain direct evidence for different magnetic structures. The results on the Gd doped samples confirm the existence of a large negative contribution to both the Se and Eu hyperfine fields as suggested by bulk magnetization experiments but not previously observed in local studies of this system. Large changes in spin lattice relaxation are noted in increasing fields.

The magnetic compound EuSe has been known to exhibit several interesting magnetic phases below its Néel temperature of 4.6 °K [1]. Investigations of its phase diagram have been made using the technique of Neutron Scattering [2, 3] and by magnetic [4, 5, 6], optical [7] and heat capacity [1, 8] measurements. A tentative phase diagram has been proposed by Kuznia [9].

Furthermore, the introduction of rare earth impurities to EuSe is known to produce an increase in the Curie-Weiss temperature [10] and to stabilize the ferromagnetic structure in the alloys.

In this paper we present some initial results of a N. M. R. spin-echo study of the spin structure and phase diagram of pure EuSe and of the local properties of the alloys of EuSe with GdSe.

At 1.3 °K, in zero external field, we observe a spin-echo signal peaked at 57.50 MHz in EuSe which we identify with the  $\text{Se}^{77}$  nuclei. The high field dependence of the resonance frequency confirms this identification. At low temperature and in zero field, the  $\text{Se}^{77}$  line is sharp and symmetric as shown in figure 1. As an external field is applied an asymmetry develops on the high frequency side of the line and by 4.5 kG we observe two lines of about equal intensities and we note that the echo decay time  $T_2^*$  is lower for the high frequency line. A correction for this effect will produce a small change in the relative intensities observed at 4.5 kG. Above 7 kG this line shifts to lower values at a rate in good agreement with the gyromagnetic ratio of  $\text{Se}^{77}$ .

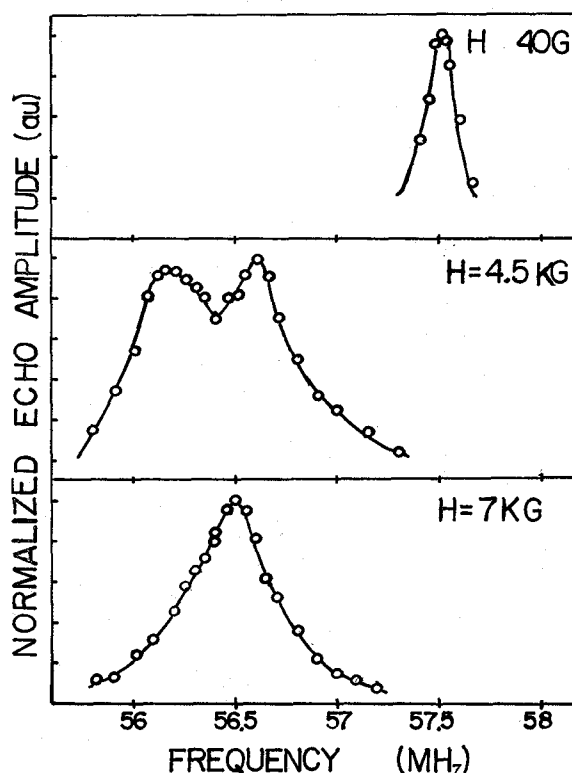


FIG. 1. —  $\text{Se}^{77}$  Spin Echo Spectra in EuSe at 1.3 °K in various external fields.

The hyperfine field at the  $\text{Se}^{77}$  nucleus is 70.7 kG and is directed opposite to the direction of sample magnetization.

(\*) Supported in part by the National Science Foundation.

In figure 2 we show the effect of temperature on the field dependence of the  $\text{Se}^{77}$  line. At 1.3 °K the asymmetry and additional line develop on the high frequency side of the original line while at 2.26 °K and above the asymmetry and the new line are on the low frequency side. No such behavior is seen in the data taken at 1.71 °K. The temperature variation of the  $\text{Se}^{77}$  hyperfine field measured in a 5 kG field indicates that in the temperature range of about 1.6 °K to 2.0 °K the  $\text{Se}^{77}$  line remains fairly symmetric.

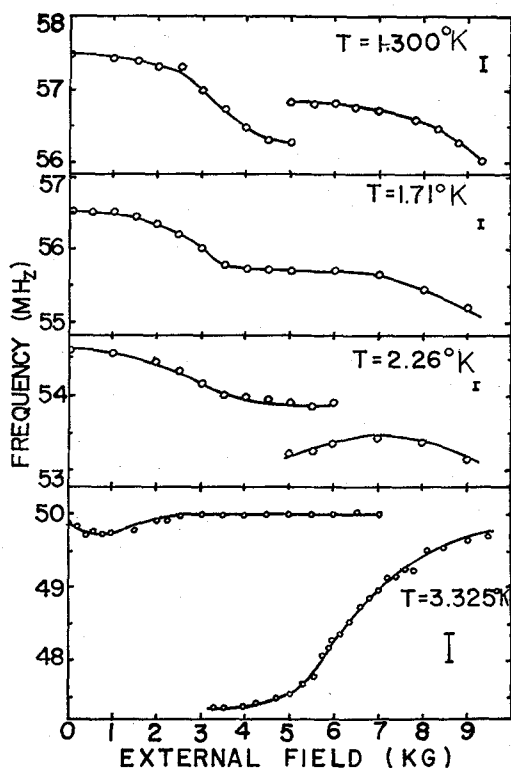


FIG. 2. — The variation of  $\text{Se}^{77}$  h. f. with the applied field at four different temperatures in EuSe.

The overall characteristics of the  $\text{Se}^{77}$  spectra and its dependence on the temperature and external field can be used to determine the regions in which the spin structure changes. As the temperature is raised the field dependence changes systematically to that shown at the highest temperature 3.84 °K. These data indicate a field induced variation in the spin structure which takes place over an appreciable field interval which roughly corresponds to that for which the two contributions are observable. At 1.3 °K a lower limit to the field is about 4.5 kG. We observe similar field variation changes in  $T_2^*$  and  $T_1$  at the  $\text{Se}^{77}$  site.

In zero field and at 1.3 °K, we observe two lines in the  $\text{Eu}^{153}$  spectrum, a strong line at  $119.1 \pm .1$  MHz and a weak line at  $131.1 \pm .1$  MHz. As the external field is applied the line at 131.1 MHz becomes relatively stronger. In fields above 4 kG the 119.1 MHz line is not observed. In fields above 8 kG, the line at 132 MHz also disappears and a new line is observed at about 143 MHz beginning at a field of about 6 kG. This line gets stronger as the external field increases and finally shifts to lower frequencies for fields greater than 13 kG. The  $\text{Eu}^{153}$  lines at low fields agree with two of the lines

reported by Kuznia [9]. However no line was observed at about 135 MHz where Kuznia [9] reported a line due to  $\text{Se}^{77}$ .

The behavior of both Eu and Se is similar in that they both indicate a change in spin structure which occurs at about 4.5 kG at 1.3 °K. This change in spin structure probably corresponds to the ferrimagnetic to ferromagnetic transition already discussed [11] for EuSe at low temperature.

In the temperature range 1.6 °K to 2.0 °K where we observe a single symmetric  $\text{Se}^{77}$  line a peak in the low field magnetic susceptibility has been reported by Schwob [12]. The relationship of susceptibility behavior to our N. M. R. results is not understood at present. Studies of the power dependence of the echo amplitude and of  $T_2^*$  indicate distinct changes in behavior at about 2.8 °K and 1.8 °K. The data shown in figure 2 for  $T = 2.26$  °K again indicate a transition in the spin structure but with a reduction in the  $\text{Se}^{77}$  hyperfine field observed at about 5 kG. The data at 3.325 °K show one additional feature, a small dip in the resonance frequency near 0.9 kG. At this temperature range the zero field spin structure is believed to be anti-ferromagnetic. However the low radio frequency field needed to excite the echo in the low field region at these temperatures does not seem entirely consistent with the structure.

In figure 3, spectra of  $\text{Se}^{77}$  in pure EuSe and in samples with GdSe are shown. The addition of 1 % GdSe causes a significant shift in the  $\text{Se}^{77}$  hyperfine field corresponding to a large additional negative contribution. Bulk magnetization measurements on these materials have been interpreted in terms of an increase in negative conduction electron polarization

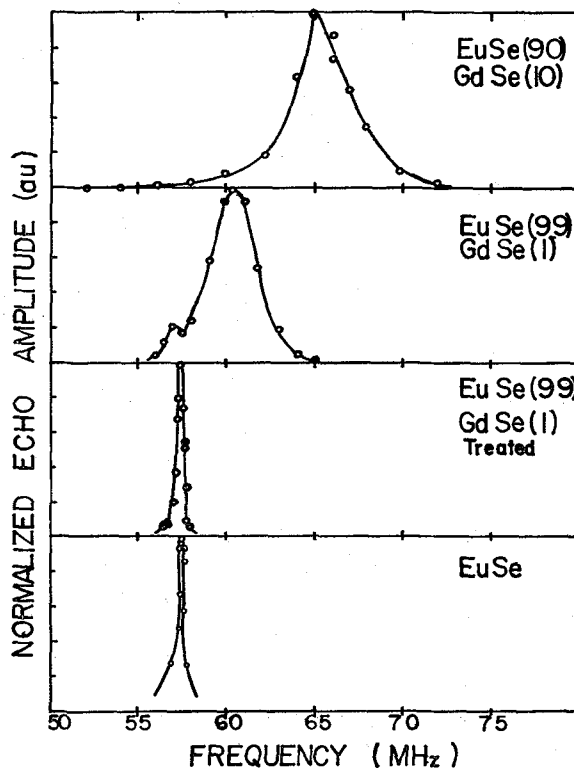


FIG. 3. —  $\text{Se}^{77}$  spin echo spectra at 1.35 °K in pure EuSe and in doped samples.

which coincides with an increase in both the electrical conductivity and the Curie temperature [10]. This effect is even more pronounced in the 10% sample. Vacuum annealing of the 1% sample is known to drastically reduce the conductivity. In the annealing process europium is removed from the lattice and leaves behind a double negative charge on a vacant site-compensating the excess positive charge from two  $Gd^{3+}$  atoms [13]. The hyperfine field at the  $Se^{77}$  nuclei in a treated sample as shown in figure 3 is restored to the value observed in pure EuSe further supporting the existence of a contribution of the hyperfine field directly correlated with the conduction electron

concentrations. Similar effects have been observed in the  $Eu^{153}$  spectra of these alloys in zero field and at 1.35 °K.

A preliminary study of the field dependence of  $T_1$  in these samples indicate some remanence of the behavior observed in pure EuSe. This might be attributed to an inhomogeneous structure present in the alloy samples or to simple sample inhomogeneities.

We are grateful to the staff of the IBM Research Center, Yorktown Heights, New York for many helpful discussions. We also appreciate the help of Mr. Dan Vona and Mr. William Rodger in this work.

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