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Abstract

In order to resolve two previous conflicting reports on detectable but weak nuclear magnetic resonance (NMR) ^{33}S signals in unenriched EuS, a sample of ^{33}S-enriched EuS was prepared and the NMR and its temperature dependence were measured in the range from 1.3 to 4.2 K. It was verified that the T=0 extrapolated NMR signal has a value of 12.73 MHz (≈ 39 kG), not 5.4 MHz, as one group had reported. The temperature dependence of the NMR was used to assess the applicability of two proposed spin-wave-region power-law schemes. The schemes attempted to systematize and explain the simple power-law behaviors measured by NMR and other techniques that have been reported (or have been present in measured data, but not reported) for more than five decades. The scheme proposed by Koebler *et al.* [Physica B **364**, 55 (2005)] contends that the low-temperature magnetization of EuS follows a simple T^2 behavior all the way up to $0.75T_c$. The ^{33}S spin-echo measurements are consistent with a power law, but cast doubt on the T^2 dependence. Possible reasons for discrepancies between various EuS NMR measurements are discussed in the paper as well as means of resolving such issues by future experiments.

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^{33}S NMR measurements in ^{33}S-enriched ferromagnetic EuS and the question of power-law behaviors

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In order to resolve two previous conflicting reports on detectable but weak nuclear magnetic resonance (NMR) ^{33}S signals in unenriched EuS, a sample of ^{33}S-enriched EuS was prepared and the NMR and its temperature dependence were measured in the range from 1.3 to 4.2 K. It was verified that the $T=0$ extrapolated NMR signal has a value of 12.73 MHz ($\approx$39 kG), not 5.4 MHz, as one group had reported. The temperature dependence of the NMR was used to assess the applicability of two proposed spin-wave-region power-law schemes. The schemes attempted to systematize and explain the simple power-law behaviors measured by NMR and other techniques that have been reported (or have been present in measured data, but not reported) for more than five decades. The scheme proposed by Koebler *et al.* [Physica B **364**, 55 (2005)] contends that the low-temperature magnetization of EuS follows a simple T^2 behavior all the way up to $0.75T_c$. The ^{33}S spin-echo measurements are consistent with a power law, but cast doubt on a T^2 dependence. Possible reasons for discrepancies between various EuS NMR measurements are discussed in the paper as well as means of resolving such issues by future experiments. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3055270]

I. INTRODUCTION

We have prepared a ^{33}S-enriched sample of EuS and have established that the ^{33}S NMR resonance has a $T=0$ value of $\approx$12.73 MHz. This result resolves the conflict between two previous reports of weak ^{33}S NMR signals in unenriched EuS.[1,2] We have also measured the temperature dependence of the NMR signal between 1.3 and 4.2 K.

The magnetic properties of EuS have been studied extensively by many techniques over several decades both in the low-temperature and in the critical regimes. Various discrepancies are still unresolved. In the critical region EuS exhibits a slightly different critical exponent β from that of its cousin EuO, which is somewhat perplexing. The differences in the behaviors of these two ferromagnets in the spin-wave regime are even more pronounced.

In the critical region, measured exponents differ by only small amounts in 3d magnetic systems, so it is sometimes difficult to determine whether this is due to discrepancies between different measurement techniques/systematic errors or to the physical properties of the magnetic systems. One might expect the same critical behavior for EuO and EuS, whereas experiments seem to show that $\beta=0.368$ for EuO but is 0.33 for EuS.[3]

The low-temperature spin-wave regime behavior of the magnetization in magnetic systems actually exhibits much more significant unexpected variations than in the critical region, although this is generally not recognized within orthodox treatments of the subject. While the analyses of NMR and other data by conventional spin-wave theory have appeared to give satisfactory results, persistent revisions of fitting parameters have invariably followed new measurements.[4–6]

By contrast, the very first precision NMR measurement on a magnetically ordered system (in $CuCl \cdot 2H_2O$) (Ref. 7) showed a simple T^4 power-law behavior within the lowest $\approx$10% of the (sublattice) saturation magnetization, at variance with the expectations of conventional spin-wave theory. A simple power-law behavior (T^2) was again reported at low temperatures in some of the europium chalcogenides (EuO, EuS, and EuSe).[8] In other cases, such as in the chromium trihalides,[9] Davis and Narath appeared to have been completely unaware of the power-law behaviors that are clearly present in their data (see, for example, the simple power-law behavior of $CrBr_3$ in Fig. 1, which is fitted extremely well by $T^{1.718\pm0.004}$). Such simple power-law behaviors seem to suggest that there is something amiss with conventional theory, and may be an indication that the conventional view of the fundamental magnetic interactions in insulating solids (and possibly metals as well) may not be quite correct.

Such an assertion has been championed for well over a decade now by Koebler *et al.*[10,11] In the scheme Koebler *et al.*, devised, the underlying magnetic interactions are attributed to non-Heisenberg higher-order spin or multispin interactions, and the allegedly resulting power laws are seen to consist of integral or half-integral powers of the temperature ($\Delta M \propto T^{1.5}$, T^2, $T^{2.5}$, etc). For the case of EuS, Koebler *et al.* contend that the magnetization follows a simple T^2 behavior all the way up to $0.75T_c$. In the case of $CrBr_3$, it is claimed[11]

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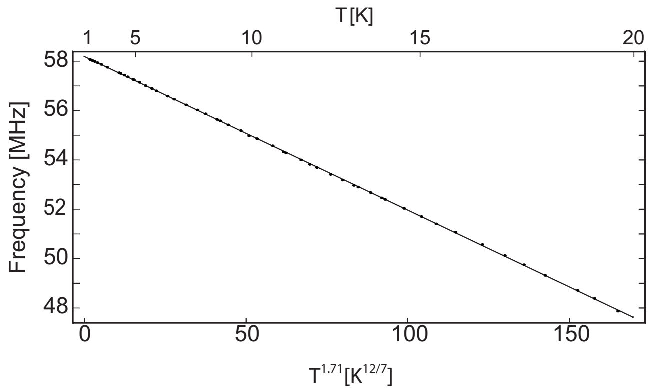

FIG. 1. NMR temperature dependence of $CrBr_3$ as a function of $T^{12/7}$.

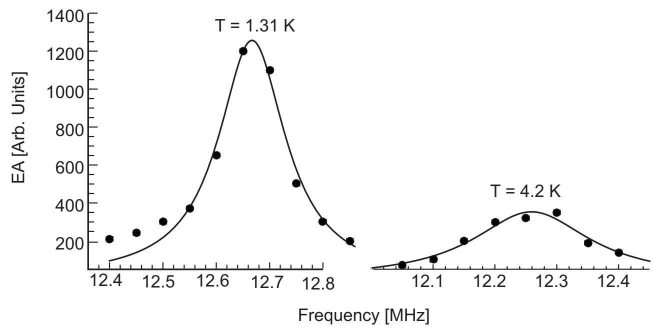

FIG. 2. ^{33}S spin-echo envelopes at the highest and lowest measured temperatures.

that the behavior exhibits a "crossover" from one T^2 behavior at the lowest temperatures to another T^2 behavior at higher temperatures. Looking at the results depicted in Fig. 1, it is difficult to accept the validity of this analysis, since the very high precision $CrBr_3$ NMR data of Davis and Narath display a very clear $T^{1.71}$ behavior, nowhere close to T^2.

We also disagree with the characterization of Koebler *et al.* that EuS follows a simple T^2 behavior in the spin-wave regime. We do agree, however, that simple magnetic systems all seem to exhibit simple power-law behaviors in the spin-wave regime (which we will define as the region from M_0 to $\approx 90\% M_0$). Bykovetz[12,13] also devised a scheme to systematize the power laws determined from precise NMR data, as well as some high-precision macroscopic magnetization data, quite some time ago. In this scheme, the magnetization decrease at low temperatures in 3*d* ferromagnets is seen to follow one of three possible behaviors, $n=1$, 2, or 3, which are a simple function of the Heisenberg "Bloch" term, $T^{3/2}$. The three power-law behaviors are derivable from the formula $\Delta M \propto (T^{3/2})^{f(n)}$, where $f(n)=1/[1-(1/2)^n]$.[14] For $n=3$, this gives the result observed experimentally in $CrBr_3$ (Fig. 1), i.e., $\Delta M \propto T^{12/7} (=T^{1.71})$. We will argue that the behavior of the magnetization in EuS also exhibits this $T^{12/7}$ behavior, except possibly at the lowest temperatures.

To resolve the question of the validity of power-law behavior in the spin-wave regime (or to determine the validity of a specific exponent value in the critical regime), extremely precise measurements are required. For the spin-wave regime this is because the magnetization changes are small ($\approx 10\%$ or less), so that the measurement of $>0.1\%$ accuracy, and preferably $>0.01\%$, is just barely sufficient to show the validity of the power-law behavior to an accuracy of a few hundredths. It is only with such measurements that one can claim to distinguish a power-law behavior from a combination of terms such as is used in conventional theory (e.g., $aT^{3/2}+bT^{5/2}$ for ferromagnets).

The most precise determinations of the magnetization in magnetic systems have been made by performing NMR. In fact, we believe that no other measurements have sufficient precision to establish a convincing power-law behavior (except possibly for some precision flux-change macroscopic magnetization measurements). It is usually believed that the NMR frequency is directly proportional to the (microscopic) magnetization of a magnetic system, although this assumption has been repeatedly placed under scrutiny over several decades. We note, however, that the NMR technique may in some cases have potential weaknesses, such as frequency-pulling effects[3] or possibly temperature variations in the hyperfine coupling constant(s).[5] Future ^{33}S NMR measurements may help resolve such potential problematic issues in EuS and other sulphide magnets.

II. EXPERIMENT

A sample of EuS was prepared by a vapor-phase reaction of 8%-enriched sulphur with Eu metal in a quartz tube in a two-zone furnace. The ^{33}S content of this sample was thus just over 10 times the natural abundance of ^{33}S. X-ray diffraction measurements showed no detectable impurity lines and the usual EuS lattice constant of 5.969 Å.

Spin-echo measurements[15] were made with a two-pulse sequence at a repeat frequency of 16 Hz. Sample echo amplitudes (EAs) are shown in Fig. 2. The measured data points consisted of (1.31 K, 12.667 MHz), (2.02 K, 12.595 MHz), (2.60 K, 12.523 MHz), (3.08 K, 12.450 MHz), (3.80 K, 12.315 MHz), and (4.20 K, 12.259 MHz). The frequency uncertainties were near ± 0.004, except for ± 0.007 for 4.2 K. The temperatures are believed to be accurate to ± 0.01 K

III. RESULTS AND DISCUSSION

Two previous NMR measurements reported signals attributed to the ^{33}S resonance in unenriched EuS. Suzuki *et al.*,[1] reported a 5.4 MHz signal, whereas Raj[2] observed no resonance near 5.4 MHz, but detected a weak resonance near 12.7 MHz. Our measurements in the ^{33}S-enriched sample showed a greatly enhanced NMR signal strength and therefore substantiate the validity of Raj's assignment. The current measurements permitted a much more precise determination of the temperature dependence than in the unenriched sample. Attempts were made to see if the gyromagnetic ratio of ^{33}S could be determined for additional verification of the NMR assignment, but unfortunately the NMR signal weakened with applied magnetic field and faded out at about 9 kG.

Our temperature dependence measurements show that the ^{33}S NMR signal fitted to a single power-law gives an exponent of 1.63 ± 0.17, much closer to the exponent found in $CrBr_3$. It is unfortunate that all previously reported Eu

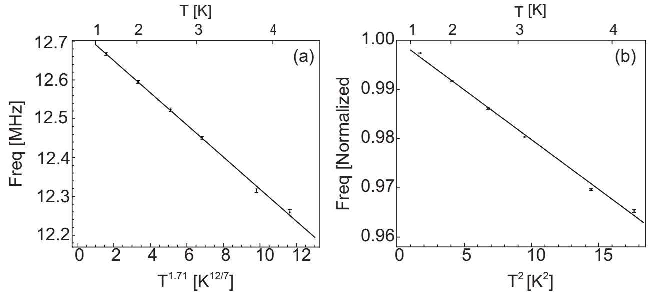

FIG. 3. (a) ^{33}S NMR temperature dependence in EuS as a function of $T^{12/7}$. (b) Comparison of the normalized ^{153}Eu NMR-frequency data of Neusser *et al.* (Ref. 5) (fitted to a T^2 dependence, shown as a straight-line curve) with the current ^{33}S NMR data points.

NMR measurements in the same sample of EuS were made either above or below 4.2 K and not throughout the entire spin-wave region. The original report of Kuznia *et al.*[8] claimed that EuS follows a T^2 dependence. However, the middle part of their data shows a curvature that is consistent with a smaller exponent than 2. Likewise, the macroscopic magnetization data points reported by Koebler *et al.*[10] show a systematic curvature that is also consistent with a lower exponent, contrary to their statement of a T^2 dependence. Fitting the numerical data reported by Heller and Benedek[3] from 4.2 to 8.16 K (i.e., below $\frac{1}{2}T_c$) gives a power-law fit of $T^{1.72}$. It must be said, however, that because of a low density of measured points, and other reasons, a rigorous statement about the validity of a simple power law cannot be made using the data of Heller and Benedek. The data show, however, that if there is a simple power-law fit below $\approx\frac{1}{2}T_c$, it is to an exponent that is smaller than 2. In Fig. 3(a), we show our ^{33}S measurements plotted as a function of $T^{12/7}$. These results are compatible with an extension of the ^{153}Eu NMR data of Heller and Benedek,[3] fitted to $T^{1.71}$, except for a small mismatch in slope. In Fig. 3(b) we plot the normalized T^2 fit of the ^{153}Eu NMR data of Neusser *et al.*[5] together with our data. Within error, our (normalized) data just barely agree, so that we cannot definitively rule out a T^2 behavior in the region below 4.2 K. In this region, the original data of Charap and Boyd[4] show a best fit to $T^{2.2}$, whereas the data of Neusser *et al.*[5] show a best fit to $T^{1.92}$. Clearly, the precision of the currently available NMR data falls just short of resolving the power-law question in this region, where ΔM changes by only $\approx 3.5\%$.

EuO, for whatever reason, exhibits distinctly different behaviors in both the critical (mentioned above) and the spin-wave regimes. In the spin-wave regime EuO appears to show[8,16] a very precise T^2 (i.e., $n=2$) behavior below $\frac{1}{2}T_c$. EuS, on the other hand, appears to behave similarly to $CrBr_3$ ($n=3$). It is, of course conceivable that EuS displays a $T^{1.71}$ behavior above 4.2 K, and a T^2 behavior below 4.2 K. Alternatively, the deviations from $T^{1.71}$ below 4.2 K could be due to either frequency-pulling effects[3] or to an alleged temperature dependence of the "transferred field" hyperfine coupling constant.[5] A measurement of the ratio of frequencies of ^{33}S to ^{153}Eu (or possibly to ^{151}Eu Eu) in one and the same sample of EuS would probably resolve these issues.

It would be very useful to carry out such measurements in EuS. The results on EuS we discussed above already suggest that the scheme proposed by Koebler *et al.*[17] may be untenable. In the case of $CrBr_3$, which is also inconsistent with the scheme proposed by Koebler *et al.*, one could, perhaps, find some explanation for their proposed crossover between two T^2 behaviors[11] (although none has been given so far), but for EuS, which is a simple, cubic system, a result showing a definitive "different than T^2" behavior would without doubt constitute a clear-cut counterexample that would put the validity of the entire scheme into question. It is thus important to resolve this issue by experimental means. Currently, it is possible to obtain 100%-enriched ^{33}S (a 12 times higher enrichment factor than our sample). Measurements with the higher enrichment are more likely to succeed in this respect and may permit an independent ^{33}S determination of the critical exponent β as well.

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[14] We note here that while these unusual formulas were derived by assuming a nonstandard behavior of the dispersion relation at low wave vector k, which in retrospect is probably not a valid assumption, all magnetization behaviors in simple $3d$ ferromagnets appear to conform to the above relations.
[15] We are very grateful to K. Raj for performing the NMR measurements.
[16] B. Birang (unpublished).
[17] See references cited in Ref. 10 and 11.