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SPIN GLASS BEHAVIOUR IN THE RARE EARTH TERNARY STANNIDE $HoRh_{1.2}Sn_{3.9}$

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Dynamic susceptibility measurements on $HoRh_{1.2}Sn_{3.9}$ have been performed in the vicinity of its magnetic transition at $T_M = 1.7$ K. $\chi'(T)$ exhibits a cusp-like peak, which is substantially depressed when an external field of a few mT is applied. Below T_M a strong frequency dependence of the susceptibility is found. The results are very similar to those of classical spin glass systems. This fact, together with an analysis of the structural disorder present in this compound, indicates also a spin glass behaviour for $HoRh_{1.2}Sn_{3.9}$. Results on other phase II ternary stannides as, e.g., the reentrant magnetic superconductor $ErRh_{1.1}Sn_{3.6}$ may be interpreted likewise.

1. Introduction

Some years ago a large family of ternary stannide compounds was found with magnetic and superconducting properties [1]. An overview of the whole family with crystal structure and transition temperature details is given in ref. [2]. We use the shorthand notation MASn for these compounds with stoichiometric formula usually written as MA_ySn_z (M = rare earth element or Y, Sc, Ca, Sr, Th; A = Co, Rh, Ru, Ir, Os; $y \approx 1.2$, $z \approx 3.6$). Most interest until now has been devoted to the compound ErRhSn, because it is a reentrant magnetic superconductor. It has a transition to superconductivity at $T_c = 1.2$ K and, when cooled further, shows a magnetic transition at $T_M = 0.5$ K, where superconductivity disappears. Almost half of the other ternary stannides undergo either a superconducting or a magnetic transition.

Within this family of stannides, two main crystal structures appear, called phase I and II. The phase II structure of ErRhSn is given in ref. [3] and from this the chemical formula $Er_xSn_{1-x}Er_4Rh_6Sn_{18}$ follows. The crystal structure is tetragonal, with space group $I4_1/acd$ and, for all the samples, twinning of the tetragonal unit cell is found. The magnetic lattice consists of tetrahedra of Er_4 centered at the sites of an fcc lattice, which will be referred as sublattice 2, and another fcc lattice of Er_xSn_{1-x} positions, to be called sublattice 1. It turns out that the partial occupation x of sublattice 1 is very sensitive to preparation conditions [4], and in this way also the transition temperatures are affected [5].

Specific heat measurements on ErRhSn show no sharp peak, which indicates the absence of long-range ordering [1,6]. From neutron diffraction measurements magnetic moments of $1.5\mu_B$ for Er^{3+} at site 2 and $3.9\mu_B$ for site 1 are found, resulting in a net moment of $14\mu_B$ per unit cell, nevertheless the large width of the individual reflections indicates that no real long-range order exists [7]. These values per Er^{3+} ions are much less than those found from Mössbauer [8] ($7.6\mu_B$) and magnetization experiments [9] ($8.7\mu_B$), and these discrepancies are still not explained.

In order to get more information on these compounds, it is interesting to study the dynamic susceptibility with varying temperature, frequency and magnetic field in the vicinity of the magnetic transition. We reported magnetization measurements on ErRhSn done in a dilution refrigerator [10]. It is known, that HoRhSn has the same crystal structure phase II and a magnetic transition at 1.7 K. In ref. [5] we showed, that the Ho and Er compounds have the same kind of be-

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haviour with respect to magnetic dilution, and we may expect, that similar magnetic interaction mechanisms are present.

In the following sections the details of the experimental results on HoRhSn are explained. At the same time, a comparison is made with classical spin glass systems, showing that the main typical features appear in HoRhSn too. Finally, we make some remarks about reported results on ErRhSn, which may also be interpreted as spin glass behaviour.

2. Experimental details

The samples of HoRhSn were prepared in the standard way as described in ref. [1]. The ratio of Ho and Rh in the input material was 1 : 2, which results in phase II crystals. By means of single crystal X-ray diffraction analysis we confirmed this phase II, and we also found evidence for twinning as reported for ErRhSn.

We investigated the composition of our samples with an X-ray micro-analysis technique. In this way we found for HoRhSn a stoichiometric formula of $HoRh_{1.22}Sn_{3.92}$, which matches the chemical composition given in ref. [1]. From this a partial occupation of $x \approx 0.8$ can be deduced, in agreement with the value given in ref. [4]. We mention here, that we found $x \approx 0.9$ for our ErRhSn samples, which is far more than the value of $x = 0.3$ given in ref. [4] for samples showing the same transition temperatures ($T_c = 1.2$ K, $T_M = 0.5$ K).

The susceptibility measurements were performed on our frequency sweeping susceptometer [11]. It uses an astatic pickup coil set, which is part of a superconducting flux transformer loop. This loop couples flux into a SQUID, which is the heart of the setup. With use of an additional mutual inductor the pickup coil set is balanced and use is made of the external feedback mode of the SQUID. Measurements can be done in the frequency range from 10 mHz up to 3 kHz, by means of a digital phase sensitive detection, with frequency independent response of the setup. Also dc magnetization measurements are possible. The flux changes in the sample are induced by an astatic primary coil set with fields between 0.1 μT and 3 mT r.m.s. With a superconducting magnet in persistent mode operation, measurements in background fields are possible. The temperature range of the setup is that of a pumped He-bath, varying between 1.3 and 4.2 K. The sample used had a mass of 43.1 mg, and is mounted on a small wheel in order to allow rotation perpendicular to the direction of dc and ac fields.

3. Experimental results

Measurements of ac susceptibility were performed within the frequency range of 0.5 to 500 Hz on HoRhSn with special attention to the temperature range around the magnetic transition, near 1.7 K.

3.1. Temperature dependence of the susceptibility

The ac susceptibility as a function of temperature $\chi(T)$, for a fixed frequency and in zero field, is given in fig. 1. The main feature of the curve is the cusp-like peak near 1.74 K, which is attributed to the magnetic transition. The small step near 3.8 K is due to small inclusions of pure tin in the sample, giving a diamagnetic contribution to the susceptibility. In order to try a fit to a Curie–Weiss behaviour, we subtract this tin contribution from the lower temperature measurements, and in fig. 1 the corrected inverse susceptibility is given. For the temperature region shown here, it is seen, that a Curie–Weiss law does not hold. For a rough estimate of the magnetic moment of the Ho^{3+}-ion we used a Curie law $\chi = C/T$ and the susceptibility value at 4.2 K. The volume density of magnetic moments was calculated using the partial occupation $x = 0.8$ as found from microanalysis. Then a value of $\mu_{eff} = 8.3\mu_B$ is found, to be compared with the free ion value of $10.6\mu_B$. As we measure the external susceptibility, the maximum value equals $1/D$, where D is the demagnetizing factor of the sample. We give an indication of this value in fig. 1 for the inverse susceptibility, assuming a spherical sample.

There is a small anisotropy in the susceptibility upon rotating the sample. The anisotropy, being

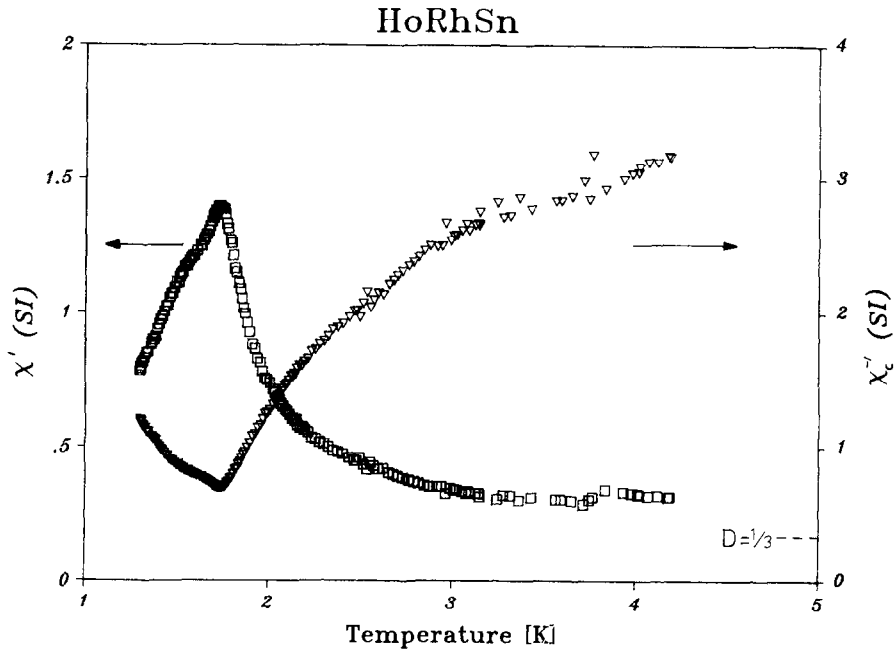

Fig. 1. Temperature dependence of the susceptibility χ' at $\nu = 112$ Hz, and of the inverse susceptibility χ_c^{-1} after correction for the tin diamagnetic contribution (see text).

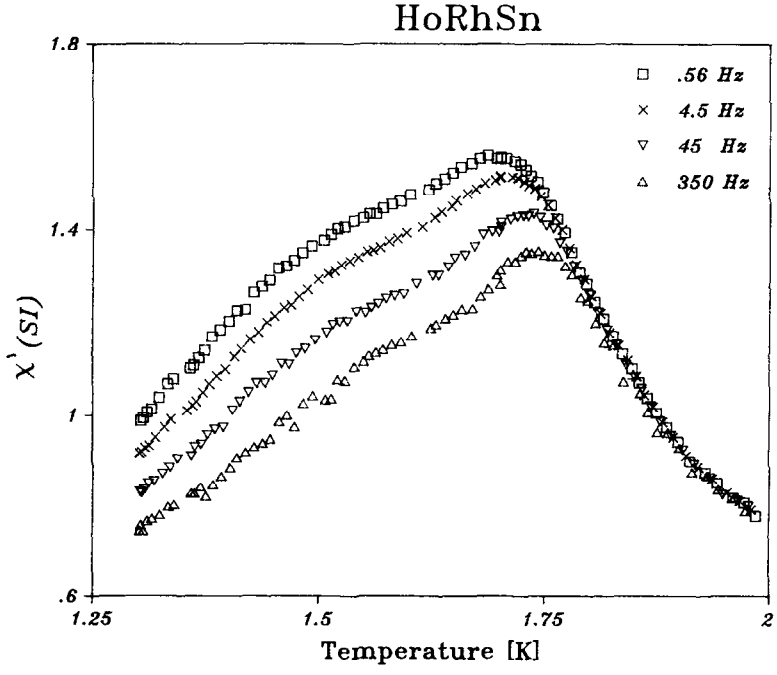

Fig. 2. Temperature dependence of the susceptibility at four different measuring frequencies as indicated.

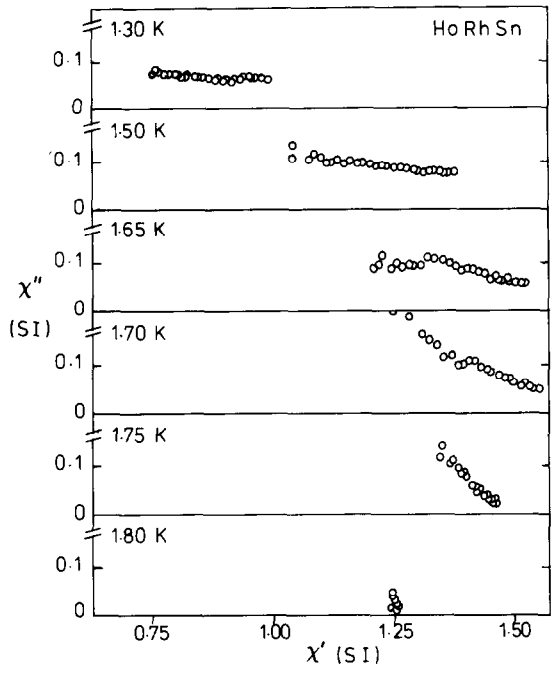

Fig. 3. Argand diagrams for HoRhSn, in the frequency range from 0.56 to 350 Hz, at several temperatures as indicated.

about 4% of the total signal at 4.2 K, increases considerably below 3.7 K. This may be understood from an irregular contribution of the superconducting tin inclusions. We assume here, that this tin has no further effects on the magnetic response of the whole sample, other than a constant diamagnetic contribution. This tin problem, which we noticed also in other publications, will be treated elsewhere.

3.2. Frequency dependence of $\chi(T)$

In fig. 2 the results for $\chi'(T)$ at four frequencies are shown. There is a strong dependence of χ' on the measuring frequency for the low temperature part and T_M is shifted to higher temperatures when ν is increased. This behaviour is typical for classical spin glass compounds as AuMn, AgMn, etc. [12]. From this fact and from more reasons explained below we identify the magnetic transition temperature (T_M) with the freezing temperature (T_f) of a spin glass. A sort of shoulder in the region around 1.5 K appears for

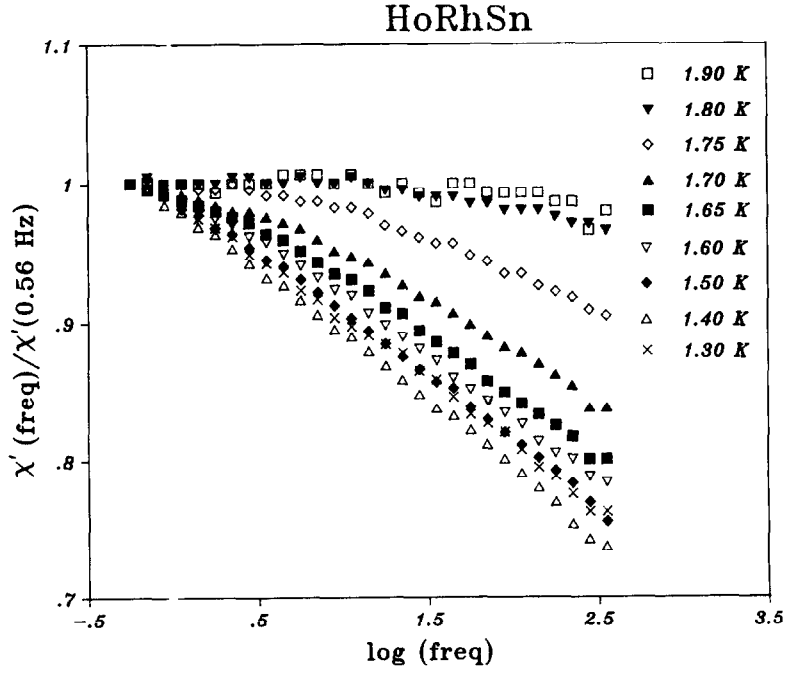

Fig. 4. Frequency dependence of the susceptibility at several temperatures as indicated. χ' is scaled to χ' (0.56 Hz) for clarity.

all the frequencies used, although it was not found in all our samples. We have no definitive explanation for its origin and it has also been found in ErRhSn [4].

Based on the data of χ' and χ'' Argand diagrams are shown in fig. 3 for several temperatures. Even though the frequency range covers only three decades, we conclude from the diagrams that they cannot be described by semicircles. This means that more than one relaxation time is involved, as found, e.g., in the spin glass $Eu_{0.4}Sr_{0.6}S$ [13].

To make a more detailed analysis, the frequency dependence of χ' is shown for several temperatures in fig. 4. Whereas in the paramagnetic region χ' is independent of ν, an almost linear behaviour of $\chi'(\log \nu)$ is found for temperatures appreciably below T_f. Within the cluster theory of spin glasses, and assuming a broad distribution of relaxation times (between τ_{min} and τ_{max}), Lundgren et al. [14] obtained the following relation between χ' and χ''

$$\chi'' = -\tfrac{1}{2}\pi\, \partial\chi'/\partial \ln \nu \qquad (1)$$

provided that $\tau_{min} \ll 1/\nu \ll \tau_{max}$, where ν is the measuring frequency. Also χ'' is then expected [14] to be almost frequency independent in the spin glass state. It seems that in our case the spectrum of relaxation times, in general temperature dependent, satisfies the above condition in some range below T_f, explaining then the linearity found in $\chi'(\log \nu)$.

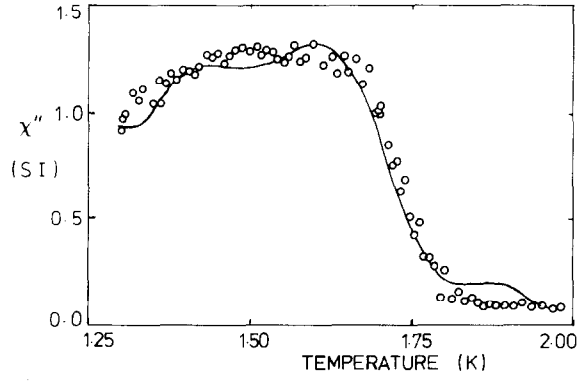

Fig. 5. Out-of-phase susceptibility of HoRhSn at $\nu = 11.2$ Hz (○). The full line represents the calculated values following eq. (1).

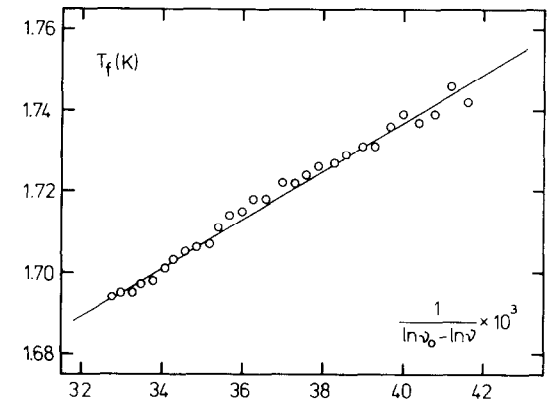

Fig. 6. Frequency dependence of the freezing temperature (T_f) of HoRhSn. The solid line represents the fit to a Vogel–Fulcher law with $\nu_0 = 10^{13}$ Hz.

In fig. 5 the results for χ'' as a function of temperature at 11.2 Hz are depicted. Near and below T_f absorption was found with similar temperature and frequency dependence as for example in AgMn [12]. A comparison with calculated values is made using the expression (1), in the same way as has been done for several other spin glasses [14,15]. As can be seen in fig. 5 the results are very satisfactory.

As T_f was found to be frequency dependent, some fittings coming from the spin glass literature were tried. An Arrhenius law does not fit the data. Instead, a Vogel–Fulcher law was employed:

$$\nu = \nu_0 \exp\{-E_a/k(T_f - T_0)\}. \qquad (2)$$

This phenomenological expression has been justified within a model of interacting clusters [16]. From the fit (fig. 6), values of 1.50 and 5.92 K are obtained for T_0 and E_a/k, respectively, when using 10^{13} Hz for ν_0. Taking T_f at, e.g., 10 Hz, reduced values $(T_f - T_0)/T_f$ and E_a/kT_f can be defined for the fitting parameters. These lie between those characteristic for well-known spin glasses [17].

3.3. Field dependence of $\chi'(T)$

Susceptibility measurements in moderate background fields have also been done in the neighbourhood of T_f. It can be seen in fig. 7 that

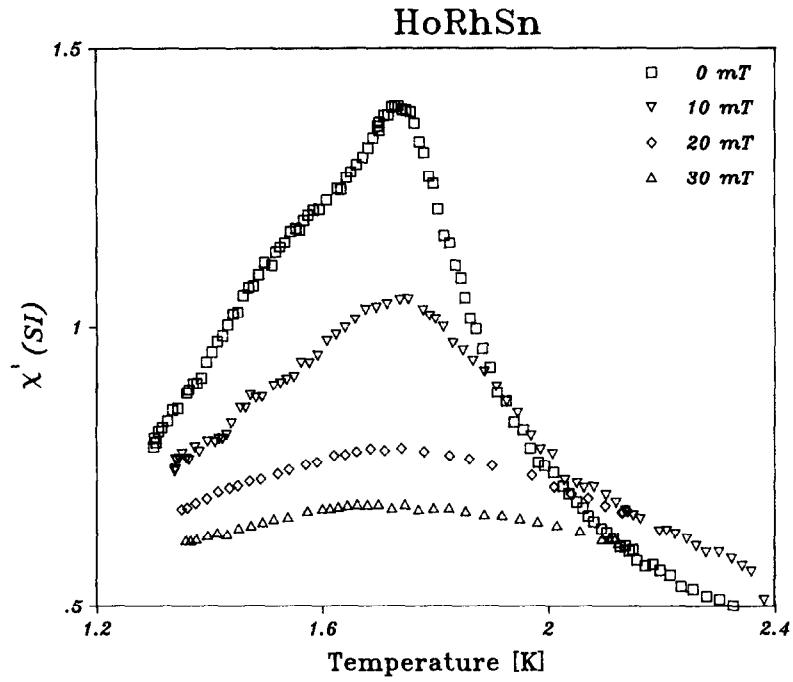

Fig. 7. Temperature dependence of the susceptibility at $\nu = 112$ Hz in several small background fields as indicated.

for fields of a few tens of mT the peak of $\chi'(T)$ is substantially lowered and broadened as found for example in AuFe [18]. The strong broadening of the $\chi'(T)$ curves makes it really difficult to derive quantitative results concerning the field dependence of T_f. In any case when increasing the field, T_f is slightly shifted to lower temperatures. The crossings in the high temperature part of the curves are due to the superconducting contribution of the tin inclusions, which is eliminated when surpassing the critical field.

4. Discussion

As it is shown throughout the paper the compound HoRhSn exhibits many characteristics of classical spin glass systems.

Summarizing:

- Cusp-like peak in $\chi'(T)$ which is depressed when a small background field is applied.
- Typical frequency dependence of $\chi'(T)$ below T_f showing basically linear $\log \nu$ behaviour within a determined range of frequencies.
- Frequency dependence of T_f following a Vogel–Fulcher law.
- Flattened Argand diagrams well below T_f.

The origin of this behaviour can be related to several possible mechanisms. In particular, there are two sources of structural disorder present in this compound. First, Ho and Sn atoms are randomly distributed in sublattice 1. The concentration fluctuations may be able to form magnetic clusters or lead to frustration effects. If this is the case we may expect the spin glass state to appear only for some range of the partial occupation x. At this time it is important to remark that our results are restricted to samples with $x = 0.8$ within an error of 0.1. The other source of disorder is the microtwinning reported for this type of compounds affecting sublattice 2. Using the same reasoning, the proportion in which the microtwin regions are distributed along the three directions of space would be very important. The same can be said about the size of these microdomains. The result is that each sublattice presents a different kind of disorder. Nevertheless, in our opinion, only one cooperative phenomenon takes place as suggested by the single feature appearing in $\chi(T)$.

The RKKY interaction, whose relevance has

already been shown for ErRhSn and HoRhSn [5], may also be a possible source of frustration because of its alternating sign. One way of discriminating among the different kind of interactions would be to play with the occupation of site 1. Previous measurements [5,19] on $Er_cY_{1-c}RhSn$ and $Ho_cY_{1-c}RhSn$, where both sublattices 1 and 2 are magnetically diluted, reveal a much stronger depression of the transition temperature than expected from molecular field theory. This fact indicates that the main interaction responsible for the transition is of short range character.

One immediately likes to make some comparison between HoRhSn and other phase II ternary stannides. All the sources of randomness mentioned for HoRhSn are present in ErRhSn making this compound a candidate for spin glass behaviour too. Specific heat measurements [6] on ErRhSn show no anomaly at T_M and a broad maximum at a temperature slightly below. In the low temperature region, after correcting for nuclear contribution, an almost linear behaviour is found. This result is similar to that reported by Fogle [20] on CuMn with the difference that there the temperature of the maximum lies above the freezing temperature. In our opinion, the expected spin glass behaviour in ErRhSn may give additional information to understand the discrepancy, mentioned in the introduction, between the values of the Er^{3+} magnetic moments. This discrepancy, not so marked, has also been found in $ErRh_4B_4$. For that case a partial disorder, not noticed in, e.g., Mössbauer measurements, is proposed as a possible explanation [21].

New experiments on HoRhSn as well as on ErRhSn will be necessary for a further support of our assertions. In particular, dc magnetization measurements are needed, which would lead to a better characterization of the time effects involved in such a viscous state. Also susceptibility measurements at higher frequencies would be desirable.

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