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Observation of a New Magnetic Anomaly below the Ferromagnetic Curie Temperature in $Yb_{14}MnSb_{11}$

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$Yb_{14}MnSb_{11}$ is an unusual ferromagnet with a Curie temperature of 52 ± 1 K. Recent optical, Hall, magnetic, and thermodynamic measurements indicate that $Yb_{14}MnSb_{11}$ may be a rare example of an underscreened Kondo lattice. We report the first experimental observation of a new magnetic anomaly in this system at around 47 K, a few degrees below T_c. Systematic investigations of the ac and dc susceptibilities of $Yb_{14}MnSb_{11}$ single crystals reveal features associated with possible spin reorientation at this temperature. This new anomaly is extremely sensitive to the applied measurement field and is absent in temperature-dependent dc magnetization data for fields above 50 Oe. The origin of this could be due to decoupling of two distinct magnetic sublattices associated with $MnSb_4$ tetrahedra.

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The family of compounds with the structure $A_{14}MnPn_{11}$, also known as "14-1-11" phases, show interesting electronic and magnetic properties ranging from paramagnetic insulating to ferromagnetic metallic behaviors depending on the type of cation A (Ca, Sr, Ba, Eu, and Yb) and anion Pn (P, As, Sb) [1–3]. Among these, $Yb_{14}MnSb_{11}$ is an interesting example of a local moment intermetallic ferromagnetic 3*d* compound and has been suggested as a precursor to a new class of 3*d* Kondo lattice materials [4]. This compound was first synthesized by Chan *et al.* [5], and it is isostructural with the Zintl compounds with the structure having 14 Yb^{2+} cations, an $MnSb_4^{9-}$ tetrahedron, a Sb_3^{7-} unit, and 4 Sb^{3-} anions. Initial studies on polycrystalline and single crystalline samples of this material indicated that the Mn magnetism is local in character with the exchange interaction between the well separated Mn^{3+} moments most likely due to conduction-electron mediated Rudermann-Kittel-Kasuya-Yoshida interactions [5,6]. The Curie temperature (T_C) is around 53 K, with robust ferromagnetic order setting in at low temperatures. High temperature magnetic susceptibility data from single crystals yielded an effective moment of $4.9\mu_B/\mathrm{Mn}$, and low temperature magnetization data gave a saturation moment close to $4\mu_B$. Both these results suggest high spin Mn^{3+} [6], which is in agreement with the Zintl concept of charge balance. However, more recent x-ray magnetic circular dichroism measurements [7] showed that Yb carries no moment, whereas a small moment exists on Sb which is antialigned with the moment on Mn, thereby reducing the total moment to $4\mu_B$ in bulk magnetization measurements [6]. Local spin density approximation calculations on $Ca_{14}MnBi_{11}$ and $Ba_{14}MnBi_{11}$ predict the presence of a polarized hole localized on the $MnPn_4$ tetrahedron lying antiparallel to the Mn moment, resulting in the net $MnPn_4$ moment being considerably reduced from the ionic Mn^{2+} value [8]. The theoretical model further proposes that the $MnPn_4$ tetrahedra in these compounds are distributed in two disjoint interpenetrating three-dimensional networks with ferromagnetic (FM) coupling within each network but much weaker coupling between the two networks.

In this Letter, we report the first experimental observation of magnetic anomalies in the real and imaginary parts of susceptibilities at around 47 K, just below the Curie temperature in single crystalline $Yb_{14}MnSb_{11}$. Systematic measurements of the temperature-dependent dc and ac susceptibilities at different applied fields and frequencies with and without the bias fields confirm that the anomalies in the susceptibility are caused by a change in magnetic nature at the characteristic temperature (around 47 K). We ascribe this to spin reorientation or change in anisotropy as reflected in the ac susceptibility and likely associated with the suggested sublattice decoupling.

Single crystals of $Yb_{14}MnSb_{11}$ were grown from a Sn flux using growth conditions similar to those discussed in Ref. [6]. The crystals were characterized using single crystal x-ray diffraction, resistivity, heat capacity, magnetization, and Hall measurements [9]. To check for reproducibility, the experimental measurements reported here were done on three different samples, including crystals grown in different batches.

The dc magnetization measurements were carried out using a physical property measurement system (PPMS). Earlier magnetic measurements on $Yb_{14}MnSb_{11}$ single crystals showed that these compounds are highly anisotropic below T_C [6]. Figure 1 shows the dc magnetization of the single crystal measured along the *c* axis of the sample. The measurements were carried out in an applied magnetic field of 1 kOe, and the inset (a) shows the inverse susceptibility as a function of temperature. The sample shows a paramagnetic behavior at high temperature and

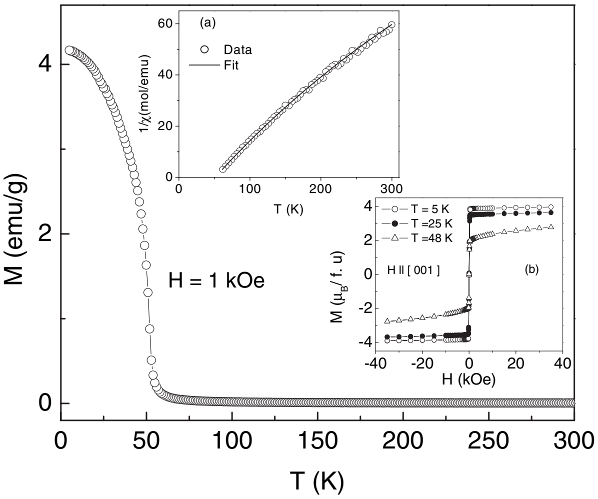

FIG. 1. Temperature-dependent dc magnetic susceptibility of $Yb_{14}MnSb_{11}$ at an applied field of 1 kOe. Inset (a) shows the fit to the modified Curie-Weiss law and inset (b) M-H at $T = 5$, 25, and 48 K measured along the c axis.

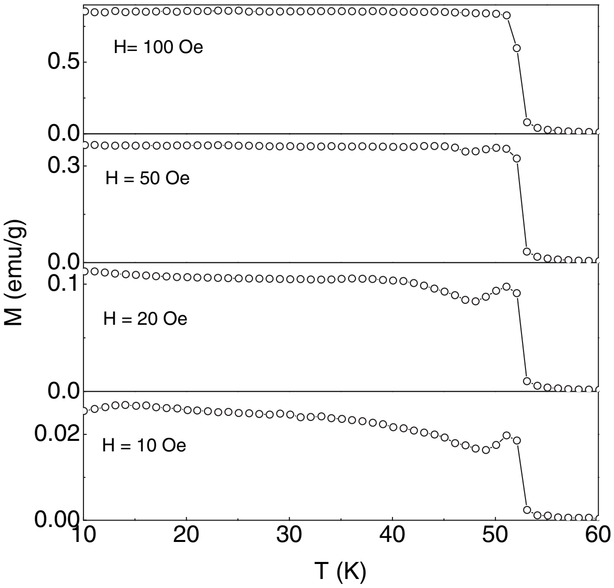

FIG. 2. Temperature-dependent dc magnetization at various H values, indicating the magnetic anomaly close to $T = 47$ K.

undergoes a ferromagnetic transition at around 52 ± 1 K. Note that, under these measurement conditions, the magnetization increase below T_C shows a classical mean-field behavior with no sign of any anomaly below the Curie temperature. The high temperature paramagnetic data (57–300 K) can be fitted to the modified Curie-Weiss law $\chi = \chi_0 + C/(T - \theta)$, which includes a temperature independent parameter χ_0 due to the Pauli and Landau paramagnetism [6]. The parameters obtained from the fit are $\chi_0 = 0.0037$ emu/mol, $C = 3.24(1)$, and $\theta = 50.9(1)$ K. An effective moment μ_{eff} of $5.09\mu_B$ is obtained from the equation $\mu_{\text{eff}} = \sqrt{7.99C}$ and is higher than the spin-only value of $4.9\mu_B$ from $Mn^{3+}(d^4)$. The Curie temperature is close to the previously reported T_C from electrical resistivity and specific heat measurements. Inset (b) in Fig. 1 shows the hysteresis loops along [001] at $T = 5$, 25, and 48 K. The coercivity (H_C) is very small and is temperature independent, indicating that the sample is a soft ferromagnet without any disorder and the measured magnetic properties are intrinsic to the sample. The magnetization saturates at $H = 300$ Oe, and the saturation moment obtained is $3.96\mu_B$ close to the expected saturation moment of $4\mu_B$ consistent with the spin-only value associated with four unpaired spins, ruling out the possibility of any magnetic response due to the other impurities such as Yb^{+3} or Sb ions [5].

The field cooled (FC) magnetization data for different dc fields in the range $H = 10$–100 Oe are shown in Fig. 2. It can be seen that, for $H \leq 50$ Oe, the FC curve shows an anomaly close to 47 K observed as a dip in magnetization. We discovered this feature serendipitously, and, as can be seen in Fig. 1, the presence of this feature is completely masked at applied fields of the order of 1000 Oe. Because of this extreme sensitivity of the susceptibility to the measurement fields, we believe that the presence of this anomaly below T_C might have been missed or overlooked in prior studies by other groups. For example, FC data for applied fields of 100 Oe or higher does not show any magnetic anomaly at 47 K and just follows a conventional monotonic mean-field variation below the Curie temperature of 52 K.

ac susceptibility with or without superimposed dc magnetic fields is a powerful probe to study the dynamic response in the vicinity of magnetic transitions in a material. The real part of the susceptibility χ' is determined mainly by the magnetic anisotropy and domain-wall energies, and the imaginary component χ'' gives the energy absorption arising due to reversible domain-wall motion. The presence of the anomalous dip in magnetization was clearly revealed when systematic ac susceptibility measurements were done at various frequencies. Detailed ac susceptibility measurements are carried out in the PPMS at different ac amplitudes ranging from 1 to 16 Oe and over frequency range 10 Hz–10 kHz. ac susceptibility measurements with fixed ac amplitude were also carried out with varying dc bias fields in the range of 0 to 1 kOe. As these measurements depend on the magnetic history of the sample, prior to each measurement the sample was heated above the ordering temperature to get rid of memory effects.

Figure 3 shows (a) the in-phase and (b) the out-of-phase parts of the ac susceptibility (χ', χ'') vs T measured with an ac amplitude of 10 Oe and without the bias field. A nearly frequency-independent peak is seen at 51 K coinciding with the FM-PM transition. The peak is a result of competition between the increase in the spin-spin correlation length, which diverges as temperature approaches the

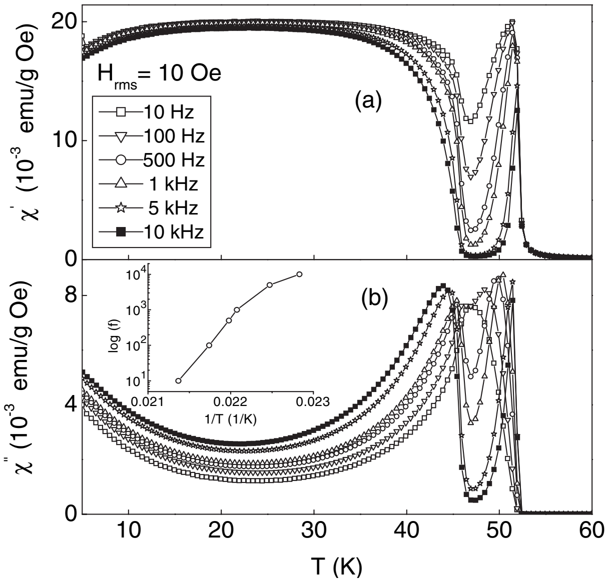

FIG. 3. Real (χ') and imaginary (χ'') parts of the ac susceptibility at different frequencies measured at an rms field amplitude of 10 Oe. The inset shows the logarithm of the frequency vs the inverse temperature for the χ'' peak.

Curie point and limited by the formation of magnetic domains just below T_C. The position of the maximum at 51 K is also independent of the amplitude of ac field. As the temperature is decreased further, there is a sharp drop in susceptibility with a minimum ($\chi_{\min}$) at a lower temperature (47 K for $f = 10$ Hz), which is frequency dependent. What is surprising, though, is that, below the minimum which occurs in the temperature range 50–45 K, χ' increases sharply as the temperature is decreased further and at around 35 K tends to be constant down to 15 K, below which χ' decreases again. Such an increase in susceptibility at low temperatures is reminiscent of the behavior in many reentrant systems [10]. The drop in susceptibility becomes more pronounced, and $\chi_{\min}$ shifts to lower temperatures and broadens as the frequency is increased.

χ'' [Fig. 3(b)] also shows an interesting trend. At low frequency ($f = 10$ Hz), χ'' has a single peak at around 47 K (the temperature at which $\chi_{\min}$ is observed in χ') and drops to zero close to the FM-PM transition. This peak shifts to higher temperatures as the frequency is increased (from 47.2 K at 10 Hz to 51.4 K at 10 kHz), and a second peak emerges. The second peak becomes more pronounced and shifts to lower temperatures with increase in frequency. The frequency dependence of the second peak is plotted as an inset in Fig. 3(b). Similar to χ', the width of the minimum in χ'' increases with increase in frequency. In general, a nonzero χ'' is associated with dissipation from domain-wall movement, and the drop in χ'' can be understood in terms of pinning of the domain-wall motion [11]. Note that the eddy current contribution calculated from the resistivity data in Ref. [5] is negligible in these compounds. In order to rule out the possibility of demagnetization effects, the ac susceptibility measurements were carried out at different ac amplitudes, and the features in the real and imaginary component of susceptibility were confirmed to be present even for ac amplitude of 1 Oe.

The behavior of the ac susceptibility is further analyzed by plotting the data (Fig. 4) in the complex plane as χ'' versus χ' at different temperatures in which each frequency represents a point. The Cole-Cole equation for the complex linear susceptibility is given by

$$\chi(\omega) = \chi_s + \frac{\chi_0 - \chi_s}{1 + (i\omega\tau_c)^{1-\alpha}},$$

where χ_0 and χ_s are the isothermal and adiabatic susceptibilities, respectively, τ_c is the median relaxation time, and α determines the width of the distribution [12]. It can be clearly seen from Fig. 4 that, for all the frequencies in the temperature range close to the minimum in the susceptibility curves (45–50 K), the susceptibilities shift from a nearly isothermal limit through the maximum to almost adiabatic values, indicating that the corresponding relaxation process slows down. It is important to note that this shift is not present at the PM-FM transition but only at lower temperature, where the magnetic anomaly is located, and, close to the Curie temperature, the susceptibilities shift back to the isothermal region. This indicates that a change in relaxation process occurs around the characteristic temperature where the new magnetic anomaly is observed.

To further investigate this anomalous susceptibility behavior, the ac susceptibility was also measured in the presence of a dc bias field, and it was observed that the magnitude of the susceptibilities (both real and imaginary)

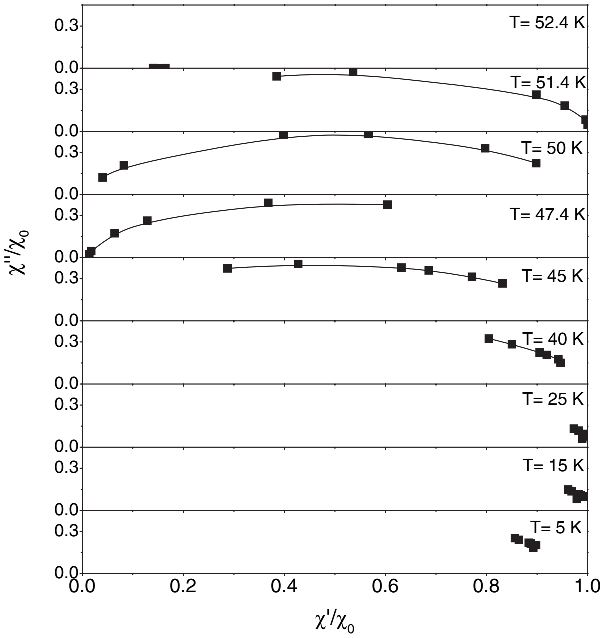

FIG. 4. Cole-Cole plot of susceptibility at different frequencies.

gets suppressed in the presence of the dc magnetic field. The low amplitude ac magnetic field is just a weak perturbation in this case and cannot alter the domain formation established by the applied dc magnetic field.

We point out possible scenarios that could account for the observed magnetic anomalies. At first glance, these features appear to be due to temperature-induced domain-wall motion under excitation of the ac field. Domain dynamics is expected to be influenced by wall pinning mechanisms or a sudden change in anisotropy of the basal plane, which results in an increase in coercivity as in the case of hard ferromagnets. Similar anomalies in χ'' have been reported in hard ferromagnets such as $Nd_2Fe_{14}B$ and R_2Co_{17} ($R = \mathrm{Tb, Dy, Ho}$) single crystals and interpreted due to spin reorientation and change in magnetic anisotropy, respectively [13,14]. It was modeled that sudden change in anisotropy can induce pinning of the domain walls either by the surface or by grain boundaries [13]. Minima in χ' and χ'' close to the Curie temperature as in the present experiments have also been observed in uniaxial ferromagnets such as $BaO_6Fe_2O_3$ and $SrFe_{12}O_{19}$ [15] and interpreted as due to domain-wall relaxation from Bloch type to linear type walls. However, while there are qualitative similarities, it is unlikely that the spin-reorientation mechanisms in soft magnetic $Yb_{14}MnSb_{11}$ are the same as in hard magnets. Domain-wall pinning and movement can be effectively ruled out in our case in light of the following observations: (1) The coercivity does not show any strong temperature dependence. (2) These single crystals have very little disorder to favor domain pinning. (3) Measurements done with the dc field applied in different orientations show that the anomalies are present and there is no dependence on crystallographic direction.

Our results can be put in perspective with the magnetic behavior of a couple of other systems belonging to the same class. Two transitions in susceptibility were reported in $Yb_{14}MnBi_{11}$ single crystals [5]. In that system, the FM onset occurs at 55 K, and a second transition at 28 K was attributed to spin reorientation due to either structural or electronic transition. The dc susceptibility data on $Yb_{14}ZnSb_{11}$ show a broad maximum at 85 K, and, for temperatures below 20 K, the susceptibility increases with decrease in temperature, resulting in a $\chi_{\min}$ below T_C similar to the one observed in the present work [16]. This has been explained in terms of intermediate Yb valence [15]. Recent x-ray photoelectron spectroscopy (XPS) measurements on a $Yb_{14}ZnSb_{11}$ sample revealed the presence of Yb^{3+} and Yb^{2+} $4f$ states in the valence band region, confirming the intermediate valence of Yb in this compound. However, XPS measurements on a $Yb_{14}MnSb_{11}$ sample showed the absence of Yb^{3+} states in the valence band [17]. As pointed out earlier, based on the low temperature hysteresis measurements, we can rule out the possibility of Yb^{3+} impurities in our samples.

The drop in χ' and χ'' observed in $Yb_{14}MnSb_{11}$ can be understood in the framework of a recent theoretical model [8]. According to this model, $MnPn_4$ tetrahedra should be considered as units responsible for the magnetism in this compound instead of Mn ions. These magnetic units are distributed between two different networks with ferromagnetic coupling within each network and antiferromagnetic coupling between different tetrahedra. The relevant length scale is not the Mn-Mn distance but the Pn2-Pn2 distance, which, in turn, determines the hopping along the Mn-Pn-Mn-Pn chains. The energy difference between the FM and the antiferromagnetic ground states is very small. We propose that the observed minimum in susceptibility measured along the c axis in this soft ferromagnetic $Yb_{14}MnSb_{11}$ is most likely associated with the disruption of the weak ferromagnetic coupling between the two sublattices by the ac field just below T_C. Since the magnitude and the sign of the coupling between the two sublattices is very weak and sensitive to material parameters [8], it is likely that the coupling also depends on temperature and appears to be weakest a few degrees below T_C.

Given the interest in $Yb_{14}MnSb_{11}$ as a precursor to $3d$ Kondo lattice materials, our discovery of a new magnetic anomaly in this system underscores the importance of revisiting the problem of magnetic interactions in metallic ferromagnetics.

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