Anisotropic spin-glass-like and quasi-one-dimensional magnetic behavior in the intermetallic compound Tb_2PdSi_3

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We report temperature-dependent ac susceptibility (χ) measurements on a high-quality single crystal of Tb_2PdSi_3, crystallizing in a AlB_2-derived hexagonal structure. This compound is found to exhibit features attributable to quasi-low-dimensional magnetism at high temperatures and anisotropic spin-glass-like behavior at low temperatures (< 10 K) with an unusually large frequency dependence of peak temperature in ac $\chi(T)$. This compound thus presents a novel situation in metallic magnetism, considering that the former phenomenon is normally encountered only among insulators, whereas the anisotropic spin-glass-like behavior, to our knowledge, has not been known in stoichiometric intermetallic compounds.

The field of magnetism continues to be an exciting one due to the discovery of magnetic materials with unusual characteristics leading to the discovery of novel phenomena. In recent years, there has been a tremendous increase of activity on materials with magnetic frustration effects leading to spin-glass freezing[1] on the one hand, and with low-dimensional effects[2] on the other. As far as spin-glass freezing is concerned, it has been generally assumed that this phenomenon is isotropic in stoichiometric compounds. With respect to low-dimensional magnetism, the focus has always been on insulators in which the magnetic ordering is mediated by superexchange mechanism via the intervening nonmagnetic atoms. However, the existence of low-dimensional effects, to our knowledge, has not been demonstrated among *intermetallic* compounds. The existence of a compound with these properties in a metallic environment would be surprising, as the indirect exchange interaction via the conduction electrons in metals, being of a long-range type, is expected to destroy low-dimensional character in favor of three-dimensional interaction. In this article, we bring out that the intermetallic compound Tb_2PdSi_3 exhibits certain unusual strongly anisotropic features in the temperature (T) dependent ac susceptibility (χ), both above and below long-range magnetic ordering temperature (close to 24 K), which appear to have some bearing to the above assumptions.

This compound crystalizes in a AlB_2-derived hexagonal structure.[3] It is worthwhile stating that the Pd-based ternary compounds R_2PdSi_3 (R = rare earth) have been found to exhibit many interesting and unusual magnetic and transport properties.[4–16] The properties of the Tb compound are particularly notable. While the reader may see Refs. 6 (on polycrystal) and 12 (on single crystal) for many other interesting properties of this compound, we recall here only those which are relevant to the present article. All the results conclusively establish that long-range magnetic ordering sets in below about 24 K. However, the nature of the magnetism appears to be very complex with a strong evidence for the existence of ferromagnetic correlations along basal plane and antiferromagnetic interplane interaction (along the c direction); the

moment orientation appears to be on the basal plane. In addition, the dc χ data reveal one more transition below about 10 K in the polycrystal,[6] whereas the data for the single crystal reveal[12] more transitions at lower temperatures depending on the orientation and the (magnetic field and thermal cycling) history of the sample. Another puzzling observation in the dc $\chi(T)$ plot is that there is a peak at about 55 K for $H//[0001]$ (where H is the magnetic field). This peak, extending over a wide temperature range, is very broad, reminiscent of that predicted for one-dimensional magnetism.[17]

The single crystalline sample employed in the present investigation is the same as that in Ref. 12. The ac χ measurements were performed in the T interval 2–150 K at various frequencies ($\nu = 1.2$, 12, 120, and 1220 Hz) for two crystallographic orientations $[10\bar{1}0]$ and $[0001]$ with respect to the direction of the ac field (2 Oe) on the same piece employing a commercial (Quantum Design) superconducting quantum interference device.

The results of ac χ measurements are shown in Figs. 1 and 2 for the two orientations. It is distinctly clear from Fig. 1 that there is a peak at 23.6 K in the real part (χ') of ac χ and the peak temperature is independent of ν. This establishes that the compound undergoes long-range magnetic ordering, but not spin-glass ordering, at 23.6 K. The corresponding feature (appearing as a kink at the same temperature) is extremely weak for $H//[0001]$. There is also a peak in the imaginary part (χ'') for $[10\bar{1}0]$ at the same temperature, but considering that the peak position is ν independent, one must conclude[1] that the anomalies at 23.6 K do not originate from spin-glass freezing.

The first observation of emphasis is that, as T is lowered, one observes another peak around 10 K for $[10\bar{1}0]$ for the lowest ν both in χ' and χ'' and the peaks move towards a higher temperature, say, from 10 to 14 K as the ν is varied from 1.2 to 1200 Hz (unlike the 23.6 K transition) (Fig. 1). At this juncture, it may be stated that the neutron diffraction data on polycrystalline material[10] reveal the presence of a
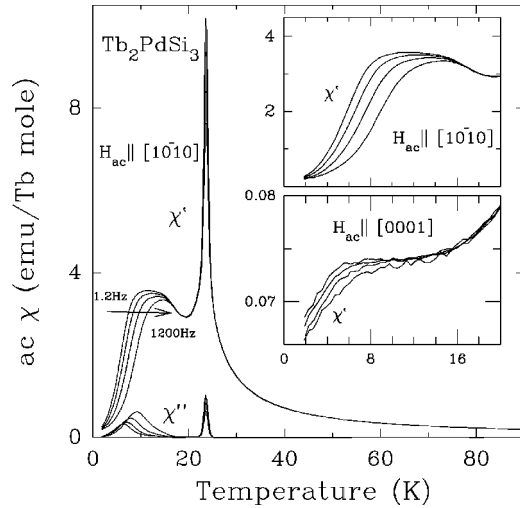
FIG. 1. Temperature dependent ac susceptibility (χ) behavior at various frequencies for single crystalline Tb_2PdSi_3 for $H//[10\bar{1}0]$. χ' and χ'' represent real and imaginary parts, respectively. The transitions below 10 K are compared in the insets (one below the other) for two directions. The direction of the shift of the curves for $T < 15$ K with increasing frequency (1.2, 12, 120, 1220 Hz) is shown by an horizontal arrow.

spin-glass-like component along with the long-range ordering, which actually prompts us to attribute this frequency dependence to spin-glass-like freezing. But, in Ref. 10, both the orderings are proposed to set in at the same temperature (close to 24 K), whereas in the present study, we observe only long range ordering at 23.6 K with the spin-glass-like features appearing only at 10 K. We believe that this discrepancy arises from the differences in the degree of Pd-Si disorder among these two forms of the material (more in the polycrystalline form)—a finding interesting in its own right. Though this frequence dependence is characteristic of spin glasses, it is hard to conclude[18] for such anisotropic concentrated magnetic systems whether the transition is of a spin-glass type. For this reason, we call this behavior "spin-glass-like." If these properties are truly due to spin-glass behavior, this anomaly in such a stoichiometric compound might arise due to the triangular arrangement of Tb ions (topological frustration) and/or a small degree Pd-Si disorder (see below for a discussion on crystallographic features). In any case, if this feature in this compound is isotropic, one should make similar observations in the data for $H//[0001]$. In sharp contrast to this expectation, we do not see (Fig. 2) any peak in the T range 7–12 K for this direction. Thus, the anisotropic nature of the 10 K feature makes this compound an interesting one. However, the $\chi'(T)$ curve for the latter direction shows a drop at a lower temperature, say around 5 K, for $\nu = 1$ Hz. In other words, the former direction shows a spin-glass-like feature at about 10 K, whereas the latter orientation shows similar frequency-dependent χ' features around 5 K (see the inset of Fig. 1). These findings (low-T transitions at distinctly different temperatures for these two directions) are rather consistent with the features in the zero-field-cooled dc χ data of Ref. 12 [compare Figs. 2(a) and 2(b) of Ref. 12]. The above 5 K feature in any case cannot be attributed to
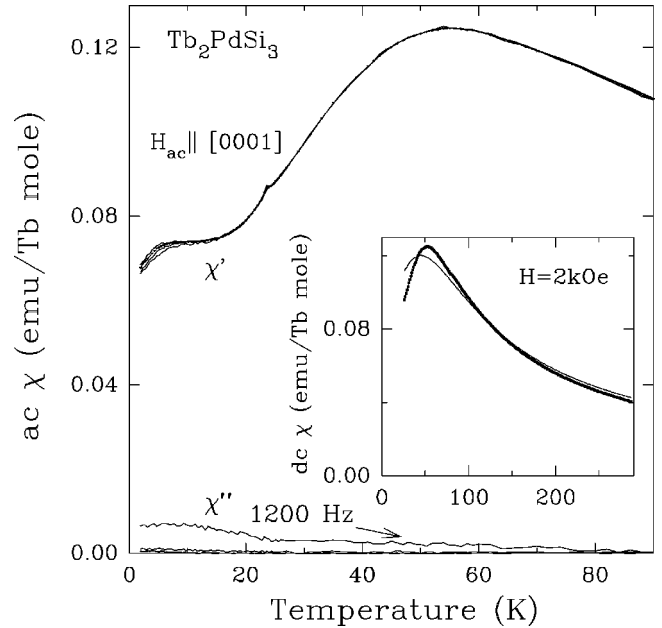

FIG. 2. Temperature dependent ac susceptibility (χ) behavior for various frequencies for single crystalline Tb_2PdSi_3 for $H//[0001]$. χ' and χ'' represent real and imaginary parts, respectively. The peak temperature in χ' for the low-temperature transition shifts to a higher temperature with increasing frequency (1.2, 12, 120, and 1220 Hz) (shown in an expanded form in the inset of Fig. 1). The χ'' is featureless in the entire temperature range with negligibly small values for lower frequencies. The inset shows the dc χ behavior (Ref. 12) above 25 K with the continuous line representing a fit as described in the text.

"canonical spin-glass" behavior,[1] as the sign of the magnetoresistance in the vicinity of 5 K [see Fig. 2(b) of Ref. 12] for $H//[0001]$ is opposite (positive) to that expected for spin glasses, and that $\chi''(T)$ does not apparently exhibit a sharp feature, however, weak it may be, around 4 K. Needless to emphasize that the magnitude of the shift (>2 K) of the peak temperatures with ν for these transitions is interestingly very large compared to that known (about 1%) for canonical spin glasses. It is not out of place to mention that we have also measured the isothermal magnetization (M) and we find that M varies esssentially linearly for $H//[0001]$ without any hysteresis at low fields (below 20 kOe), say at 5 K, as reported in Ref. 12, whereas for $H//[10\bar{1}0]$, the M-H plot exhibits a hysteresis loop. Therefore, if the hysteresis in M for the latter orientation arises from spin-glass-like anomaly, then clearly this behavior is anisotropic.

In order to bring out the second major point of emphasis, we turn to the data above 23 K. It is obvious that the $\chi'(T)$ exhibits a broad peak around 55 K for [0001] as in the case of dc χ (T) plot (see the inset of Fig. 2, with the data taken from Ref. 12). This feature is so broad that it can not result from spin-glass freezing of some fraction of Tb ions. The present article places this on a firm footing by reporting ac χ as a function of ν, i.e., the plots for all the frequencies overlap above 25 K.

A careful look at the crystallographic features in light of the above finding is quite intriguing. As already remarked,
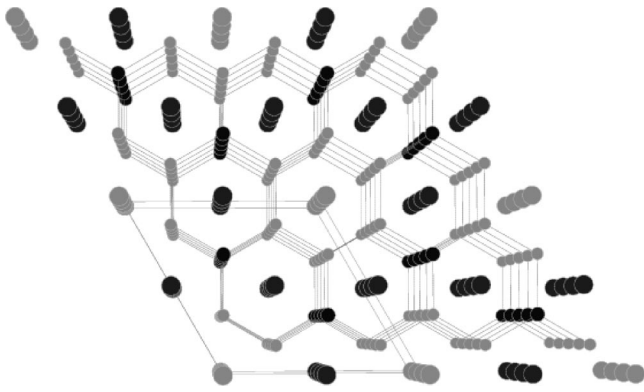
FIG. 3. The unit cell of Tb_2PdSi_3 in the a-b plane viewed along the c axis. Big cirles (light black at $2b$ site and dark black at $6h$ site) represent Tb atoms, whereas smaller ones represent Pd (darker) and Si (lighter) atoms, respectively.

this compound forms in a AlB_2-derived hexagonal crystal structure. The ternary derivative of this structure presents an interesting situation (Fig. 3) crystallographically in the event[19] that there is an ordered occupation of the B site by Pd and Si atoms in the basal plane; that is, there are two different chemical environments for R ions [called $2(b)$ and $6(h)$ sites], doubling the a parameter.[4] As a signature of this, one normally observes superstructure lines in the x-ray diffraction pattern [e.g., (101) and (110) appearing at $2\theta = 16.6$ and 21.7 Å, respectively, with CuK_α radiation]. However, such superstructure lines are usually weak (the intensity of which apparently depends upon the degree of Pd-Si disorder). Hence these can easily escape detection. Thus, the wavelength of the neutron employed in a previous study[10] on the polycrystalline form is too large (2.44 Å) that these lines could not be detectable, whereas, in the x-ray diffraction pattern recorded with a much smaller wave length radiation (CuK_α) on the same polycrystalline sample, we could observe these lines in agreement with a previous article[3] reporting doubling of the a parameter. While finalizing this article, we came to know that careful neutron diffraction investigations[20] on the single crystals indeed reveal the doubling of the a parameter. The R and Pd-Si layers are stacked alternately along the c direction and the arrangement of R ions in the basal plane is triangular. The R ions at the $6(h)$ site are sandwitched by eight Si atoms and four Pd atoms (with four Si and two Pd placed on the vortices of the hexagon on each side) along the hexagonal tube, whereas the ones at the 2(b) site are sandwiched by hexagons of Si in the immediate vicinity. Thus there are chains of R ions at the

center of the hexagonal tube made up of Pd and Si atoms and the R-R distances are of the order of 4 Å. It has been established[4] that the R chain at the 2(b) site can undergo magnetic ordering due to finite interaction among 2(b)-2(b) chains (which are at a distance of about 8 Å from each other) leaving the intervening R ions at the $6(h)$ site paramagnetic. We therefore attribute the broad 55 K peak in χ to the antiferromagnetic correlations within the chain of Tb ions present at the $2(b)$ site, and the observed broad peak is similar to that predicted theoretically by Bonner and Fischer[17] several years ago. In order to compare the experimental χ behavior with a model on low-dimensional systems, for instance, as in Ref. 21), we have used the dc χ data (Ref. 12) (above 25 K) instead of ac χ, as the absolute values are more reliable in the former case. We obtained a fairly good fit (see continuous the line in the inset of Fig. 2 as per the equation 2 in Ref. 21) for an exchange interaction strength of about 35 K. The broad peak is, however, not observable for $H//[10\bar{1}0]$ (see Fig. 1). It is to be remarked that the strength of this peak for $H//[0001]$ is very low in the dc χ as well.[12] Such a weak feature is masked for $H//[10\bar{1}0]$ as the χ values for the paramagnetic Tb ions at the $6(h)$ site for this orientation are large increasing at a faster rate (than the decrease of χ below 45 K in the other direction) with decreasing T. It is worth noting that the paramagnetic Curie temperature is widely different (-30 and 23 K for [0001] and $[10\bar{1}0]$ directions), unlike the situation for other analogous heavy rare-earth compounds.[11,14,16] Such a strong anisotropy even in the paramagnetic state is also a characteristic of quasi-one-dimensional magnetic systems.

To conclude, Tb_2PdSi_3 apparently exhibits quasi-one-dimensional features in the magnetic susceptibility data (around 55 K), thereby characterizing this compound, to our knowledge, to be the first one among intermetallics to show this phenomenon. Naturally, this compound will thus serve as an ideal model system to evolve theories to understand low-dimensional magnetism dominated by indirect exchange interaction via conduction electrons (unlike the situation up to now in insulators in which the superexchange interaction mediates magnetic coupling) and associated interchain coupling effects. Another unusual observation is that, the 23.6 K long-range magnetic ordering is followed by "anisotropic" spin-glass-like anomalies at lower temperatures; in addition, there is a large frequency dependence of the peak temperature in the ac $\chi(T)$ plot, uncharacteristic of canonical metallic spin glasses. These results clearly reveal that this compound is an exotic magnetic material.[22]

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[22] Looking at the similarities of the properties with those of Ca_3CoRhO_6 as the T is lowered [that is, quasi-one-dimensional magnetism (55 K) to long-range ordering (23.6 K) to disordered magnetism (below 10 K) coupled with a large frequency dependence of ac χ around 10 K], it is even tempting to classify this compound along with the rare class of magnetic compounds, called "partiallly disordered antiferromagnetic structural" compounds. See the references, S. Niitaka *et al.*, Phys. Rev. Lett. **87**, 177202 (2001); E. V. Sampathkumaran and Asad Niazi, Phys. Rev. B **65**, 180401 (2002). It may be noted that both Ca_3CoRhO_6 and Tb_2PdSi_3 are similar structurally as well in the sense that these compounds have magnetic ions at the corners and centres of hexagons and hence are triangular lattices. Further work in this direction is urgently required to verify this interesting possibility.