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Anisotropic magnetic behavior of $PrAg_2Ge_2$—a crystal field study

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ABSTRACT

A crystal field (CF) analysis of the experimental, single crystal magnetic susceptibility data (300–1.8 K) along and perpendicular to the [0 0 1] axis, of the Ag based rare earth intermetallic compound $PrAg_2Ge_2$, has been carried out for the first time, thus yielding first reliable set of CF parameters for the system. The susceptibility feature at 12 K is possibly due to CF effects rather than the magnetic order as proposed earlier. This removes the issue of the transition temperature being too large to scale properly with the de Gennes factor. We have used the set of CF parameters to find the Stark energies of the ground state and the excited states together with their corresponding eigenvectors, and the thermal variation of the magnetic specific heat. Possible explanation of the absence of magnetic ordering of the Pr sublattice and the nature of variation of the CF parameters with the substitution of transition-metal ion in $PrAg_2Ge_2$ is studied and discussed in relation to $PrAu_2Ge_2$. All computations have been carried out using the intermediate coupling scheme including the J-mixing.

1. Introduction

Most of the rare earth intermetallic compounds having the general formula RT_2X_2 (R: rare earth ion, T: transition-metal ion, and X: p block element (Si or Ge)) crystallize in the $ThCr_2Si_2$-type of crystal structure [1] with the space group I4/mmm. They exhibit interesting magnetic properties, e.g. heavy-fermion behavior, pressure-induced superconductivity [2], unconventional metamagnetic transitions [3], valence fluctuation [4]. Hence these compounds have been investigated extensively during last four decades.

However, the studies of $PrAg_2Ge_2$ compounds are rather sparse. The measured thermal variation of average d.c. magnetic susceptibility ($\chi=(\chi_{001}+2\chi_{100})/3$) in the temperature range 400–1.7 K [5], in a magnetic field of 5 T for polycrystalline samples, reveals an unconfirmed magnetic ordering at 12 K. For this compound no long-range magnetic order was found down to 1.5 K. Szytula et al. [5] have, however, suggested that the compound is antiferromagnetic at low temperatures; although the type of magnetic ordering is not clear. Joshi et al. [6] measured the anisotropic d.c. magnetic susceptibility along the [0 0 1] and [1 0 0] axis for $PrAg_2Ge_2$ single crystals in the temperature range 300–1.8 K in an applied magnetic field of 0.1 T. Their [6] study reveals that the compound exhibit a Curie–Weiss behavior at high temperatures with the [1 0 0] axis as the easy axis of magnetization and a change in slope in the magnetic susceptibility along the [0 0 1] axis as well as a sudden drop of the same quantity along the [1 0 0] axis at 12 K.

A crystal field (CF) simulation of the magnetic properties of $PrAg_2Ge_2$ was carried out [7] using the polycrystalline data reported in [5]. The details of the crystal field study [7] are not, however, available. Besides, the CF parameters derived from measurement of the average magnetic susceptibility on polycrystalline samples are not unique. In order to ascertain the nature of proposed ordering [5,6] in $PrAg_2Ge_2$, a CF analysis of the experimental data reported by Joshi et al. [6] is, therefore, necessary.

In the present work the CF parameters for the $PrAg_2Ge_2$ have been determined for the first time from the analysis of the measured magnetic susceptibilities [6] in the direction along and perpendicular to the [0 0 1] axis of $PrAg_2Ge_2$ single crystals in the temperature range 300–1.8 K. Possible explanation of the absence of magnetic ordering of the Pr sublattice is discussed. The obtained set of CF parameters is used to find the Stark energies of the ground state and the excited states together with their corresponding eigenvectors and the thermal variation of the magnetic specific heat. A measurement of the magnetic specific heats for the system can be used to test the adequacy of the CF approach. Variation of CF parameters of $PrAg_2Ge_2$ on substitution of Ag for Au in $PrAu_2Ge_2$ [8] in relation to the lattice parameters is studied and discussed. The J mixing of the higher excited states within the intermediate coupling scheme has been taken into account.

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2. Methodology

2.1. Crystal field interactions

In $PrAg_2Ge_2$, the Pr^{3+} occupies the 2a sites with tetragonal site symmetry. Hence the CF Hamiltonian can be expressed as [9]

$$H_{CF} = B_{20}C_{20} + B_{40}C_{40} + B_{60}C_{60} + B_{44}C_{44} + B_{64}C_{64} \quad (1)$$

where C_{kq}'s are the spherical tensor operators and B_{kq}'s are the CF parameters in Wybourne notation [10]. It is in order to point out here that choice of a particular coordinate system is unavoidably connected with the calculation of the crystal field potential and the crystal field parameters. For each symmetry of the environment (except the case of the triclinic system), there is always such a particular coordinate system, called the symmetry adopted axis system (SAAS) for which the H_{CF} expansion (Eq. (1)) has its simplest form, which is different from all other systems (e.g. crystallographic axis system (CAS)) with respect to minimum number of independent parameters [9,11]. Disparate forms of CF Hamiltonian (H_{CF}) in Wybourne convention have been used by various authors for different hosts/systems. A list of papers reporting orthorhombic and lower symmetry non-standard CF parameter sets, which are intrinsically incompatible with the standard ones, is provided in Appendix 2 in Ref. [12]. Some of these data sets create confusion concerning the CF parameters and the operator notations particularly in the cases of low symmetry (tetragonal II (C_4, S_4, C_{4h}), trigonal II (C_3, S_6), hexagonal II (C_6, C_{3h}, C_{6h}), and monoclinic (C_2, C_{1h}, C_{2h})) [11]. These inconsistencies have been discussed in detail and a clarification of the intricate aspects was provided by Rudowicz et al. [11]. Confusion regarding the operator notation arises from the inconsistent use of the phase convention $(C_{kq}+(-1)^qC_{k-q})$ or $(C_{k-q}+(-1)^qC_{kq})$ [13]. For $PrAg_2Ge_2$, the site symmetry around Pr^{3+} being tetragonal, CF parameters with even q are admissible by group theory and no such problems are encountered here. For high symmetry cases, like the present one, where imaginary terms in the CF Hamiltonian are not involved, there exists at least one set of three mutually perpendicular local site symmetry axes, which can be chosen to coincide with the x, y, and z axes. The uniqueness of such choice for tetragonal type I symmetry has been discussed in detail by Rudowicz et al. [14]. However, for lanthanide systems where the rare earth ion is in a site of low symmetry, due to different possible orientations of the CF axes [11], different CF parameter sets can be found, which can yield identical energy levels. For Eu^{3+} in gadolinium gallium garnet, where Eu^{3+} ion is at a site of D_2 symmetry, Gruber et al. [15] had chosen the CF z-axis parallel to any one of three orthogonal C_2 symmetry axes and found six alternative sets of crystal-field parameters which could yield identical energy levels. For $TbAlO_3$, where Tb^{3+} ion is at a site of monoclinic (C_s) symmetry, three sets of CF parameters were obtained by Gruber et al. [16] from spectroscopic and magnetic susceptibility studies, which were shown [17] to be physically equivalent and correspond to the specific choice of coordinate system. The matrix elements of the operators C_{kq}, computed using standard procedure [18], are used to set up the CF Hamiltonian matrix, which is diagonalized to obtain the energy eigenvalues and the corresponding eigenfunctions. The first and the second-order Zeeman energies of the Stark states, $W_{njm}(1)$ and $W_{njm}(2)$, were obtained using the interaction $\mu_B\vec{B}\cdot(\vec{L}+2\vec{S})$ with the magnetic field $\vec{B}$ parallel and perpendicular to the CF z-axis. The values of the magnetic susceptibilities along the [0 0 1] and [1 0 0] axis were finally computed with the well-known susceptibility expression of Van Vleck [19] following the usual procedure [20]. The CF strength parameters are defined in terms of rotational invariants of the crystal field [21] as

$$S_k = \sqrt{1/(2k+1)\left[\{B_{k0}\}^2 + 2\sum_{q=1}^{k}\{(\mathrm{Re}B_{kq})^2 + (\mathrm{Im}B_{kq})^2\}\right]} \quad (2)$$

The CF strength parameters have a deeper meaning in view of Noether's theorem [22]. They are invariant with respect to an arbitrary rotation of the axis system. Hence, they can be used as a quantitative measure of the strength of the CF interaction of a particular rare earth ion in a given host. Another useful property of the quantities S_k is that they provide an additional check of the reliability of fitting of the experimental CF parameters as well as of the consistency of the transformed CF parameters expressed in different axis systems. For intricate problems with low symmetry, the computations are more involved and have been considered in detail by Rudowicz et al. [11–13].

2.2. Magnetic specific heat

Magnetic contributions to the specific heat (C_S) due to the rare-earth ions (also called the Schottky specific heat) can be obtained by subtracting the lattice contribution (C_{Latt}) from the total specific heat (C_P). Due to the variation of the electronic population in various low lying Stark levels, the magnetic specific heat C_S shows its characteristic thermal variation [20]. The variation of C_S with temperature has been computed using the relation [20]:

$$C_s = \left(\frac{R}{Z^2}\right)\left[Z\frac{\sum_i E_i^2\exp(-E_i/kT)}{k^2T^2} - \sum_i\{E_i^2\exp(-E_i/kT)\}^2\right] \quad (3)$$

where $Z=\sum_i\exp(-E_i/kT)$ is the partition function and E_i's the energies of various Stark states. The anomaly in the specific heat at low temperatures arising out of phonon, magnon or nuclear effects [23] has not been considered here.

2.3. Calculation of the CF parameter

Using a least square fit to the observed [6] thermal variation of $\Delta\chi(=\chi_{001}-\chi_{100})$, where χ_{001} and χ_{100} are the magnetic susceptibilities along the [0 0 1] and the [1 0 0] axis, B_{20} has been estimated as $-162\ \mathrm{cm}^{-1}$ using Bleaney's relation [24]:

$$\chi = -N\frac{\mu_B^2}{20(kT)^2}B_{20}g^2 <J\|\alpha\|J> J(J+1)(2J-1)(2J+3),$$

where N, g, and $<J\|\alpha\|J>$ are the Avogadro number, Lande factor, and the reduced matrix elements, respectively. For choosing the starting set of the CF parameters B_{40}, B_{44}, B_{60}, and B_{64}, we have taken a similar compound $PrAu_2Ge_2$ for which the CF parameters have already been reported [8]. The site symmetry and nearest neighbor environment around Pr^{3+} in $PrAu_2Ge_2$ and $PrAg_2Ge_2$ are similar. Substitution of Ag for Au in $PrAu_2Ge_2$ gives rises to a decrease in the lattice constant 'a' from 0.4366 nm to 0.42795 nm while the c axis is elongated from 1.0443 nm to 1.0995 nm. The c/a ratio increases from 2.392 to 2.569 and the volume is increased from 199.06 cu nm to 201.36 cu nm. Due to an increase in the unit-cell volume, a strong reduction of the Pr moment (connected with its environment) and the corresponding strength of crystal field may take place. Taking the B_{40}, B_{44}, B_{60} and B_{66} parameter values of $PrAu_2Ge_2$ as the starting parameters, final parameters are optimized using standard least squares fitting between the calculated and the experimentally determined magnetic susceptibilities at various temperatures. The obtained set of CF parameters with a good fit to the experimental [6] magnetic susceptibilities along the [0 0 1] and the [1 0 0] axis are listed in Table 1 along with the sets reported for $PrAu_2Ge_2$ [8]. The r.m.s. deviations between the observed [6] and calculated values for