

Electronic Structure of PrCo_2Ge_2

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The intermetallic compound PrCo_2Ge_2 exhibits very interesting physical properties: antiferromagnetism below $T_N = 28$ K, an order to order transition at $T_R = 8$ K, a rich magnetic phase diagram, and huge magnetocrystalline anisotropy as observed by recent experiments on a single crystal in a magnetic field up to 14 T. We performed first principles calculations based on the density functional theory. The localized $4f^2$ configuration of Pr^{3+} was treated using the open core approximation. The electronic densities of states were obtained and the position of the Fermi level was found. The hybridization between the Co-3d, Pr-5d and Ge-4p states is discussed. The calculated magnetic moment of Co is found to be quite small ($m_{\text{Co}} < 0.1 \mu_B$). The first principles calculations of the crystal field interaction were performed as well: the obtained crystal field parameters were used as the starting parameters for further refinement in comparison with experimental data of the magnetic susceptibility and specific heat. The crystal field splitting of the 4f states was determined.

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1. Introduction

The family of the RT_2X_2 (R = rare earth, T = transition metal, X = *p*-element) intermetallic compounds is one of the largest among ternary systems. In these materials a large variety of physical phenomena has been observed, among others the dense Kondo behavior, mixed valence phenomena, exotic magnetic ground states sometimes coexisting with superconductivity, which are always accompanied by very strong uniaxial magnetic anisotropy.

Majority of these compounds crystallize in the tetragonal body-centered structure (space group $I4/mmm$), which can be described as layers of atoms of the same kind stacked along the tetragonal axis in the sequence R–T–X–T. The physical, especially magnetic properties of the RT_2X_2 compounds reflect the layered nature of the crystal structure.

The early X-ray diffraction of PrCo₂Ge₂ polycrystalline sample shows [1] tetragonal crystal structure belonging to the space group $I4/mmm$.

Subsequent neutron diffraction confirmed [2] the antiferromagnetic ordering at 27 ± 1 K with propagation vector $(0, 0, 0.72)$.

In this work we present the first principles calculations of the electronic structure and crystal field using density functional theory. The comparison with our single crystal susceptibility and specific heat data is provided.

2. Method of calculations, results, and discussion

We used state-of-the-art computational methods for the electronic structure calculations, namely the full-potential linearized augmented plane waves method (LAPW, WIEN2k code) [3]. The Kohn–Sham equations were solved within the local-spin-density approximation (LSDA) [3] and the generalized gradient approximation (GGA) [3]. The relativistic effects of the valence states were treated within the scalar relativistic approximation [3], core states were described using a four-component fully relativistic Dirac solver. The correlated $4f$ states of Pr were treated in the open core approximation, and thus, the praseodymium $4f$ states are characterized by an integer occupation number $4f^2$. The number of APW, k -points, and the Fourier coefficients were carefully checked to ensure convergence of the calculations. The first principles crystal field calculations were performed using the method described in Diviš et al. [4].

The calculated electronic density of states (DOS) of PrCo₂Ge₂ for the experimental lattice parameters in normal paramagnetic state is shown in Fig. 1a. The first region, from -11.1 eV to -7.6 eV, consists mainly of the Ge- $4s$ states, which are split off from the main valence band group (see Fig. 1d). There is a band gap from -7.6 eV to -5.3 eV. The bottom of the main valence band group is situated at -5.3 eV. This band group between -5.3 eV and 2 eV represents mainly the cobalt $3d$ states with the major part located below the Fermi level (E_F), forming a pronounced broad maximum in the DOS curve between -5.3 eV to -0.55 eV, a quasigap situated below E_F , and a secondary maximum just above E_F . There is some hybridization between the Co- $3d$ (see Fig. 1c), Pr- $5d$ (see Fig. 1b) and Ge- $4p$ (see Fig. 1d) states present between -3 eV and the E_F and a pronounced contribution originating from the interstitial region (see dashed line, Fig. 1d). The energy position of the localized $4f^2$ ($j = 5/2$) states is below E_F .

E_F is situated at the end of the quasigap between the two pronounced maxima in the DOS. The orbital analysis of the DOS shows that mainly the Co- $3d$, Pr- $5d$, and Ge- $4p$ states contribute to the total value of DOS at the E_F . The value of the DOS at E_F is too small to cause the spontaneous magnetic polarization of the Co- $3d$ states. The peculiar position of E_F corroborates the idea that the absence of the cobalt magnetic moment is due to the itinerant character of the Co- $3d$ states connected with the position of E_F at the quasigap. The value of the DOS for PrCo₂Ge₂ and LaCo₂Ge₂ at the E_F corresponds to $\gamma = 9.8$ mJ/(mol K²)

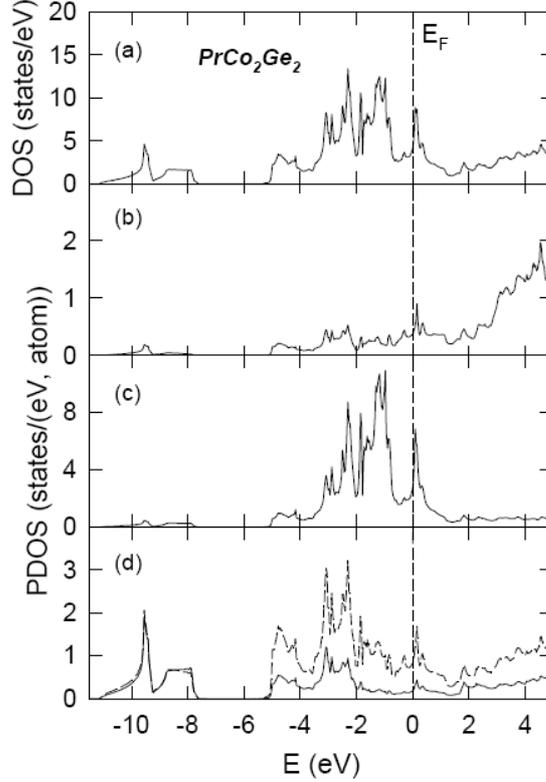


Fig. 1. The total DOS (a) and atom projected DOS (b), (c), (d) of PrCo_2Ge_2 .

and $11.1 \text{ mJ}/(\text{mol K}^2)$, respectively, which is lower than the γ value obtained from the analysis of our specific heat data for LaCo_2Ge_2 . This points to a rather low value of the mass enhancement coefficient $\lambda = 0.48$ for LaCo_2Ge_2 which is related to a small electron-phonon interaction in the RCO_2Ge_2 compounds.

In the case of LaCo_2Ge_2 the minimization of the total energy with respect to volume provided $V/V_0 = 0.936$. This is the usual underestimation provided by the LSDA. We repeated the whole procedure using the GGA form of the exchange-correlation potential and found $V/V_0 = 1.004$, which demonstrates that the GGA calculations provide a much better agreement with the experimental equilibrium volume V_0 . We did not minimize the force acting on the Ge atom since the calculated force was already quite small. The fact that the GGA provided a better ground state density also suggested to perform the first principles crystal field calculations using the GGA ground state density.

For the purpose of crystal field (CF) fitting the magnetization was measured in the range 2–600 K in several magnetic fields and the magnetic susceptibility in the paramagnetic region was taken as a slope of the $M(B)$ data at constant temperature. The CF Hamiltonian in the tetragonal symmetry depends on five

CF parameters A_n^m . The first principles calculation of the CF parameters leads to the following values: $A_2^0 = 158$ K, $A_4^0 = -13$ K, $A_4^4 = 600$ K, $A_6^0 = -4.6$ K, and $A_6^4 = 61$ K using the GGA form of the exchange-correlation potential. The second-order CF parameter A_2^0 has the correct sign, which determines the easy c -axis of PrCo_2Ge_2 in agreement with experiment and with the analysis of our susceptibility data. The parameter A_6^0 has the correct sign comparing to the CF parameters resulting from analysis of susceptibility. Since the analysis of our susceptibility data is not very sensitive to the values of off-diagonal CF parameters A_4^4 and A_6^4 , there is also agreement between first principles calculation and the CF parameters obtained from the susceptibility.

We fitted the temperature dependence of the susceptibility to this model CF Hamiltonian by an explicit parameter space search and a simulated annealing procedure [5] and obtained the same results within both methods. The CF parameters are $A_2^0 = 317$ K, $A_4^0 = 49$ K, $A_4^4 = 719$ K, $A_6^0 = -85$ K and $A_6^4 = 681$ K and a constant shift 35.1 T/ μ_B . This shift corresponds to a paramagnetic critical temperature 47.8 K, in a reasonable agreement with experimental findings (taking into account the mean-field approximation). The agreement between the model calculations and experiment (susceptibility, specific heat) confirms a dominant role of crystal field effects and an important role of exchange interactions in the system.

Acknowledgments

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References

- [1] W.M. McCall, K.S.V.L. Narasimhan, R.A. Butera, *J. Appl. Crystallogr.* **6**, 301 (1973).
- [2] H. Pinto, M. Melamud, E. Gurewitz, *Acta Crystallogr. A* **35**, 533 (1979).
- [3] P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, J. Luitz, *WIEN2k*, TU Wien, Austria 2001.
- [4] M. Diviš, J. Ruzs, H. Michor, G. Hilscher, P. Blaha, K. Schwarz, *J. Alloys Comp.* **403**, 29 (2005).
- [5] W.L. Goffe, G.D. Ferrier, J. Rogers, *J. Econometrics* **60**, 65 (1994).