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Physical phenomena of the cage compounds $RE_3Pd_{20}Si_6$ (RE = Yb, Lu)

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ABSTRACT

Features of atomic rattling motion (anharmonic thermal vibrations), a phenomenon that relates to a new route for devising materials for thermoelectric applications of complex metal alloys, have been detected in certain members of the $RE_3Pd_{20}X_6$ (RE = rare-earth element, X = Si or Ge) series of compounds relating to details of their particular crystal structure. In this work, thermal properties of $Yb_3Pd_{20}Si_6$ and $Lu_3Pd_{20}Si_6$ are reported as a first account of their position with respect to atomic rattling in an attempt to demystify the conditions that favour this dynamic materials property.

1. Introduction

$RE_3Pd_{20}X_6$ is a series of rare-earth (RE) based isostructural intermetallic compounds that form with either X = Si or Ge. The structure of the unit cell in $RE_3Pd_{20}X_6$ is amenable to a cage – or clathrate – like description due to the structural environment of the rare-earth atoms. A first report on crystallographic properties of the two cerium derivatives $Ce_3Pd_{20}X_6$ [1] was followed by initial results of the physical properties of the rare-earth silicide series of compounds [2]. $Ce_3Pd_{20}Ge_6$ has two successive phase transitions at low temperature, -quadrupolar at 1.5 K and antiferromagnetic at 0.75 K [3]. $Ce_3Pd_{20}Si_6$ is a Kondo lattice with an enormously enhanced electronic density of states [4] and a magnetically ordered ground state that has not been clarified to date [5].

The presence of thermally activated rattling motion of rare-earth atoms situated on the tetrahedral symmetry 4a-site cage in $RE_3Pd_{20}X_6$ was brought to light by results of ultrasonic attenuation measurements of the elastic constants in both the nonmagnetic compound $La_3Pd_{20}Ge_6$ [6] and in magnetic $Ce_3Pd_{20}Ge_6$ as well [7]. Interestingly, in the two Si derivatives no ultrasonic dispersion could be found [8].

2. Experimental and results

We synthesized $Yb_3Pd_{20}Si_6$ (YbPS) and $Lu_3Pd_{20}Si_6$ (LuPS)—two compounds in which the atoms occupying the rare-earth cage sites are much reduced in ionic size from that of their La- or Ce counterparts. A standard arc-melting procedure was used with stoichiometric quantities of the reactant elements (metal purity in weight percent: Lu, Yb, Pd, 99.99; Si, 99.9999) in LuPS, whereas a solid pellet of YbPS was first prepared by sintering stoichiometric quantities of the elements at 900 °C for 3 h, followed by quenching the sintered pellet in air. Powder diffraction analyses revealed a straightforward comparison with the expected cubic $Fm-3m$ space group. The lattice parameter values (12.1280(5) Å for YbPS and 12.1180(5) Å for LuPS) are significantly reduced compared to those of the two known atomic rattling compounds (12.482 Å for $La_3Pd_{20}Ge_6$ [3] and 12.4453(4) Å for $Ce_3Pd_{20}Ge_6$ [1]). Physical and magnetic properties were measured using a commercially available PPMS system from Quantum Design. The magnetic susceptibility of YbPS measured in a field of 0.1 T (not shown) gives paramagnetic Curie–Weiss behaviour from 300 K down to 20 K with a nearly free-ion Yb^{3+} effective moment value of μ_{eff} = 4.43(3) μ_B/mol Yb and a small paramagnetic Weiss temperature amounting to θ_p = −4.0(2) K. There are no indications of cooperative effects in $\chi(T)$ down to 1.9 K.

Fig. 1 displays the specific heat of LuPS and YbPS in the format C/T^3 vs. T—a presentation that is commonly used to identify the presence of Einstein optical modes in the lattice heat capacity.

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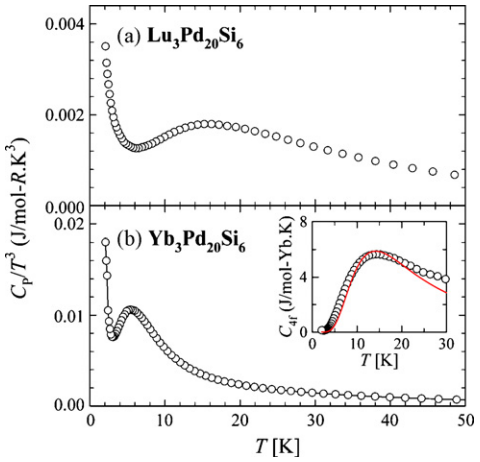

Fig. 1. Low-temperature specific heat of (a) $Lu_3Pd_{20}Si_6$ and (b) $Yb_3Pd_{20}Si_6$ plotted in the form C/T^3 vs. T to expose the presence of optical lattice vibrational modes. The inset in (b) is a plot of the magnetic 4*f*-electron derived specific heat of $Yb_3Pd_{20}Si_6$ with a fit (solid line) of a two-level Schottky expression, suggesting a crystal-electric field doublet in this compound at $\Delta_{CEF}/k_B = 37$ K above the ground state.

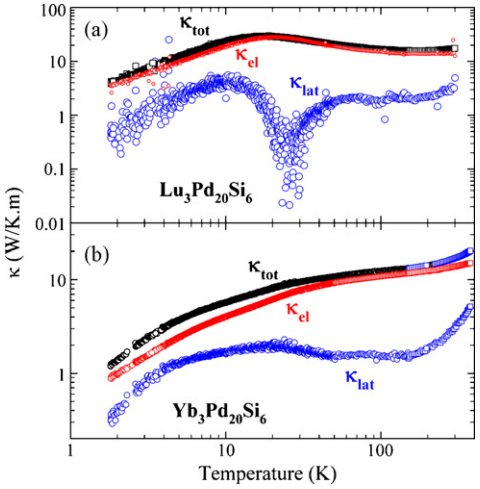

Fig. 2. Total measured thermal conductivity (κ_{tot}), electronic part (κ_{el}) and lattice part (κ_{lat}) of (a) $Lu_3Pd_{20}Si_6$ and (b) $Yb_3Pd_{20}Si_6$ plotted on log-log scales.

Qualitatively the same for both compounds, C/T^3 of LuPS shows a broad peak at $T_{max} = 15$ K for which the Einstein temperature amounts to $\theta_E \approx 5T_{max} = 75$ K, whereas in the magnetic YbPS this resonance is much sharper and at a lower $T_{max} = 5.4$ K yielding $\theta_E = 27$ K. In a crystal field environment of cubic symmetry, the $4f^{13}$ multiplet of Yb^{3+} is expected to split into two doublets and a quartet CEF state. The inset in Fig. 1(b) scales the magnetic 4*f*-electron derived specific heat of YbPS according to a two-level Schottky expression, yielding an energy separation of $\Delta_{CEF}/k_B = 37$ K, presumably for the first doublet above the ground state. Further analysis of the CEF energy level dispensation in YbPS awaits inelastic neutron scattering measurements since the low-temperature specific heat of this compound conceals, aside from possible low-lying CEF excitations, the optical lattice vibrational modes as well.

As seen in Fig. 2(a), the measured thermal conductivity $\kappa_{tot}(T)$ of especially LuPS shows flat and featureless behaviour – typical of glassy materials – over the entire temperature range. The electronic contributions to $\kappa_{tot}(T)$ were calculated using the Wiedeman–Franz law, $\kappa_{el}(T) = L_0T/\rho$ in terms of the temperature independent Lorenz number $L_0 = 2.45 \times 10^{-8}$ W Ω K^{-2}. The electrical resistivities $\rho(T)$ of both compounds (not shown) show good metallic behaviour ($\rho(T \to 0) = 3.4$ μΩ cm and RRR = 15.8 for LuPS, $\rho(T \to 0) = 5$ μΩ cm and RRR = 10.7 for YbPS). The lattice thermal conductivities, $\kappa_{lat}(T) = \kappa_{tot}(T) - \kappa_{el}(T)$ for both compounds are quite low – about an order of magnitude lower than the total – and the bulk of the heat is evidently being conducted by the abundance of free charge carriers in these systems.

The title compounds in this work have been found to show relatively low thermal conductivities in spite of being well-behaved metals. Rattling motions of the rare-earth atoms become pronounced at low temperatures and are presumed to impact on the thermal conductivities of this class of materials by effectively scattering the heat-carrying phonons. Qualitatively similar behaviour has been found also in $Ce_3Pd_{20}Ge_6$ and $La_3Pd_{20}Ge_6$ [9]—two compounds known to exhibit anharmonic dynamics at low temperatures. Atomic rattling effects claimed for the two title compounds in this work highlight the importance of size effects of the rattling or guest atoms of a cage structure. Diminishing the electronic contribution to the overall thermal conductivity is seen as a challenge to devise thermoelectric materials. The future outlook of this work is to investigate the influence of introducing electronic correlations on atomic rattling effects.

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