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Influence of hydrogenation on the magnetic properties of Er_2Ni_2Al

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The magnetic properties of Er_2Ni_2Al and $Er_2Ni_2AlH_{5.3}$ have been studied in the temperature range 2-300 K. Er_2Ni_2Al is an antiferromagnet with $T_N = 5$ K, as indicated by a pronounced maximum in the temperature dependence of the magnetic susceptibility in magnetic fields below 1 T. In the paramagnetic region, the susceptibility is described by the Curie-Weiss law, yielding an effective moment of 9.69 μ_B/Er and $\theta_p = -14$ K. The field dependence of the magnetization in the ordered state exhibits a metamagnetic transition around 2 T with a relatively wide hysteresis. The hydride $Er_2Ni_2AlH_{5.3}$ does not show any magnetic ordering above $T = 2$ K. The Curie-Weiss law fit of the magnetic susceptibility curve yields the values 9.63 μ_B/Er and $\theta_p = -10$ K. The magnetic behavior of both Er_2Ni_2Al and $Er_2Ni_2AlH_{5.3}$ is supported by the shape of the temperature dependence of the heat capacity curves. The upturn in C/T *vs.* T for $Er_2Ni_2AlH_{5.3}$, which is suppressed by an applied magnetic field, is suggestive of magnetic ordering at still lower temperatures. The dramatic suppression of Er–Er exchange interactions (the size of the Er moments is generally stable) can be understood as a consequence of H bonding, which reduces the concentration of conduction electrons.

Intermetallic / Hydride / Magnetic properties / Heat capacity

Introduction

The intermetallic compound Er_2Ni_2Al crystallizes with the orthorhombic W_2CoB_2 structure type (Pearson symbol *oI*10, space group *Immm*) [1], which is typical for a number of R_2T_2M compounds, where *R* is a rare-earth metal, *T* is Ni or Co, and *M* is Al, Ga, or Sn [2]. The magnetic properties of Er_2Ni_2Al and other related aluminides have so far only been studied above the temperature of liquid nitrogen [1]. The reported paramagnetic behavior of the magnetic susceptibility of Er_2Ni_2Al was described by the Curie-Weiss law with an effective moment of $\mu_{eff.} = 9.94$ μ_B/Er and paramagnetic Curie temperature $\theta_p = 23$ K. The authors claimed the existence of an induced magnetic moment on the Ni atoms, besides the regular 4*f*-magnetism for heavy rare-earths in the R_2Ni_2Al series. More attention has been paid to the magnetic properties of W_2CoB_2-type stannides, which exhibit a variety of magnetic phases. Ce_2Ni_2Sn was classified as a magnetically ordered Kondo system with $T_N = 4.7$ K and $T_K \approx 8$ K, and a commensurate collinear antiferromagnetic structure [3,4]. While moving further through the rare-earth series, the R_2Ni_2Sn compounds (*R* = Nd, Sm, Gd, Tb) exhibit a number of sequential magnetic phase transitions [5], the complexity of which is reflected in the magnetic phase diagram of Nd_2Ni_2Sn, which contains four different magnetically ordered phases [6].

It was recently found that compounds crystallizing with the W_2CoB_2 structure type are able to absorb large amounts of hydrogen [7]. Al-containing compounds absorb H already at extremely low hydrogen pressures (of the order of magnitude of millibars), forming hydrides with H concentrations approaching 6 H/f.u. The hydrogenation of Er_2Ni_2Al ($a = 4.1499$, $b = 5.3654$, $c = 8.2487$ Å, $V = 183.66$ Å^3) results in a strongly anisotropic lattice expansion to the composition $Er_2Ni_2AlH_{5.3}$ ($a = 3.841$, $b = 6.383$, $c = 9.106$ Å, $V = 223.3$ Å^3, $\Delta a/a = -7.4\%$, $\Delta b/b = 18.9\%$, $\Delta c/c = 10.5\%$, $\Delta V/V = 21.6\%$) and considerable shifts of the Ni atoms (Wyckoff position 4*h* (0,*y*,½), $y = 0.2368$ for Er_2Ni_2Al and $y = 0.3036$ for $Er_2Ni_2AlH_{5.3}$) towards Al atoms (2*a* (0,0,0)). Consequently, the metal substructure of the hydride is closer to the related K_2PtS_2 structure type.

So far the studies of hydrogenation-induced variations of the magnetic properties of R_2T_2M compounds have been focused on compounds crystallizing with the Mo_2FeB_2 structure type [8,9]. The rare-earth containing compounds absorb up to 8 hydrogen atoms per alloy formula unit, and a general tendency towards weakening of the magnetism is observed. On the contrary, for the uranium compounds, for which the upper limit of hydrogen content is 2 atoms per formula unit, hydrogenation results in more pronounced magnetic properties.

The investigation of the impact of hydrogenation on the magnetic properties of Er_2Ni_2Al is the first attempt to expand our knowledge about the hydrogenation properties of R_2T_2M compounds to intermetallics with the W_2CoB_2 structure type. Taking into account the substantial changes in the interatomic distances and atomic environment upon hydrogenation, a consequent impact on the electronic properties is expected. The aim of the present work was to determine the magnetic behavior of Er_2Ni_2Al at low temperatures and its changes upon hydrogenation.

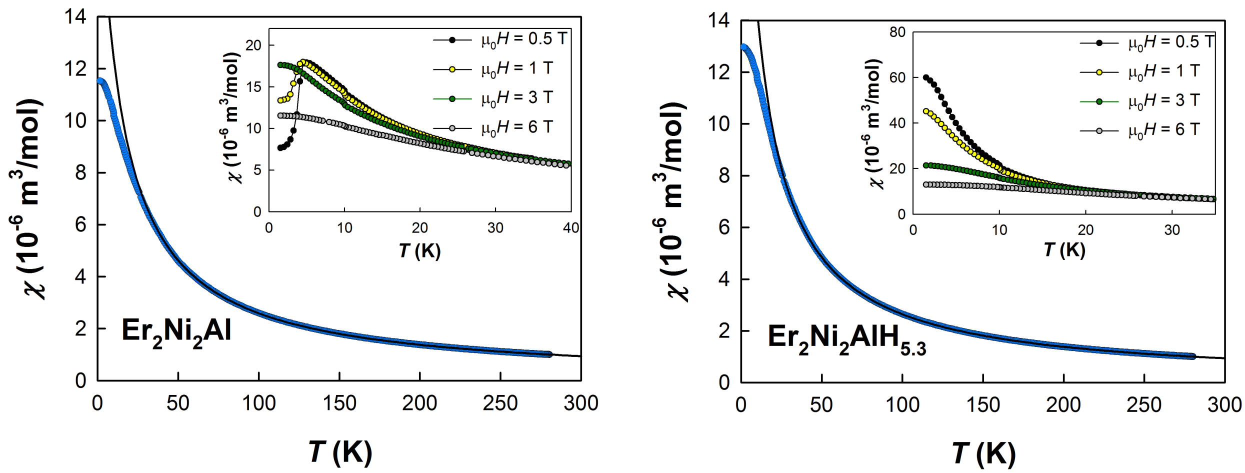
Experimental

The intermetallic Er_2Ni_2Al compound was synthesized by arc-melting stoichiometric amounts of elemental metals of purity at least 99.9% under argon atmosphere. The hydride $Er_2Ni_2AlH_{5.3}$ was prepared by exposing the activated intermetallic compound to hydrogen gas at a pressure of 0.8 atm at room temperature. The stoichiometry of the obtained hydride was determined from the amount of absorbed hydrogen. Phase analysis of the synthesized samples was carried out by X-ray powder diffraction (Bruker D8 Advance diffractometer, Cu $K\alpha$ radiation, 2θ range 10-120°, step 0.02°). Details of the synthesis of the hydride and the crystal structures of both the parent intermetallic and the hydride were reported in [7].

Quantum Design PPMS equipment was used for the magnetic studies and heat capacity measurements. Magnetic measurements of Er_2Ni_2Al and its hydride were performed in the temperature range 2-300 K and fields up to 14 T on randomly oriented fixed powder. Taking into account the decrepitation of the sample upon hydrogenation, a special treatment was required to perform the heat capacity studies. For Er_2Ni_2Al the heat capacity was measured on a bulk piece, but in the case of the hydride, on a pellet obtained by pressing the powder. The heat capacity curves were obtained without external magnetic field and in magnetic fields up to 6 T, down to the temperature $T = 2.5$ K.

Results

The temperature dependence of the magnetic susceptibility of Er_2Ni_2Al, studied in various magnetic fields, showed that the compound is an antiferromagnet with a Néel temperature of $T_N = 5$ K, which is reflected as a pronounced maximum of the susceptibility measured in a magnetic field of $\mu_0H = 0.5$ T (Fig. 1a). An increase of the applied magnetic field above 1 T results in the disappearance of the maximum, and the susceptibility becomes monotonous. In the paramagnetic region the susceptibility is described by the Curie-Weiss law, yielding the effective moment 9.69 μ_B/Er and paramagnetic Curie temperature $\theta_p = -14$ K. The value of the effective magnetic moment agrees well with the value of the free Er^{3+} ion (9.59 μ_B). The negative θ_p-value indicates dominating antiferromagnetic exchange interactions. The field dependence of the magnetization in the ordered state exhibits a metamagnetic (spin-flip) transition in the range 1-3 T with a relatively wide hysteresis and no remanent magnetization (Fig. 2). A second metamagnetic process starts at 6 T and is not completed at 14 T, the maximum field applied here. The moment reached in 14 T, 6.5 μ_B/Er, indicates that in any case parallel moment orientation is not reached.



(a) (b)

Fig. 1 Temperature dependence of the magnetic susceptibility of Er_2Ni_2Al (a) and $Er_2Ni_2AlH_{5.3}$ (b) measured in a magnetic field of $\mu_0H = 6$ T. The solid lines show the Curie-Weiss law fit. The insets present the field dependence of the magnetic susceptibility in the low-temperature range.

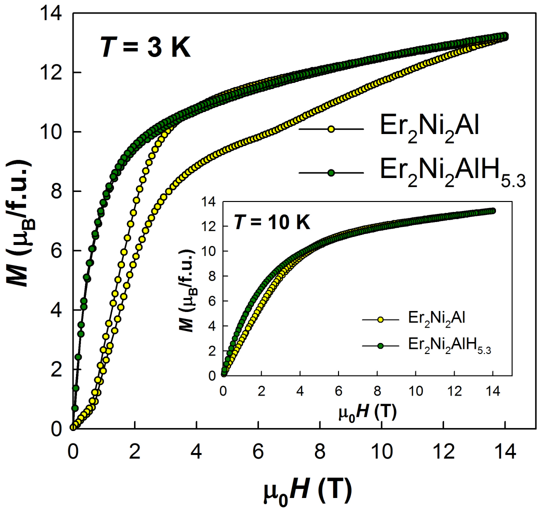


Fig. 2 Magnetization curves for Er_2Ni_2Al and $Er_2Ni_2AlH_{5.3}$ measured at $T = 3$ K. The inset shows the magnetization curves obtained at $T = 10$ K.

In addition, the low total moment (the theoretical moment of Er is 9.0 μ_B) can be attributed to crystal electric field effects and related anisotropy. This is supported by the fact that even the magnetization measured at $T = 10$ K, *i.e.* above the magnetic phase transition, which adopts the shape of the Brillouin function, does not reach the value of the fully saturated moment.

On the contrary, the hydride $Er_2Ni_2AlH_{5.3}$ does not show any magnetic ordering above $T = 2$ K (Fig. 1b). The upturn of the magnetic susceptibility observed in a magnetic field of $\mu_0H = 0.5$ T is suppressed by applying higher fields. The magnetic susceptibility curve can be described by the Curie-Weiss law, yielding the values 9.63 μ_B/Er and $\theta_p = -10$ K. As it can be seen, the hydrogenation practically does not affect the value of the effective moment on the erbium atoms and leads to a slightly less negative paramagnetic Curie temperature, indicating weakening of the antiferromagnetic exchange interactions. The magnetization curve measured at $T = 3$ K shows a tendency to saturation, however, similarly to Er_2Ni_2Al, the maximum applied magnetic field of 14 T is not enough to reach the value of fully ordered magnetization for the Er^{3+} ions (Fig. 2). At $T = 10$ K, the slope of the magnetization curve is less steep and above $\mu_0H = 5$ T the curve practically coincides with the one measured for the parent intermetallic.

The magnetic phase transition in Er_2Ni_2Al appears as a pronounced sharp λ-type anomaly in the temperature dependence of the heat capacity $C(T)$ at $T = 5.3$ K (Fig. 3).

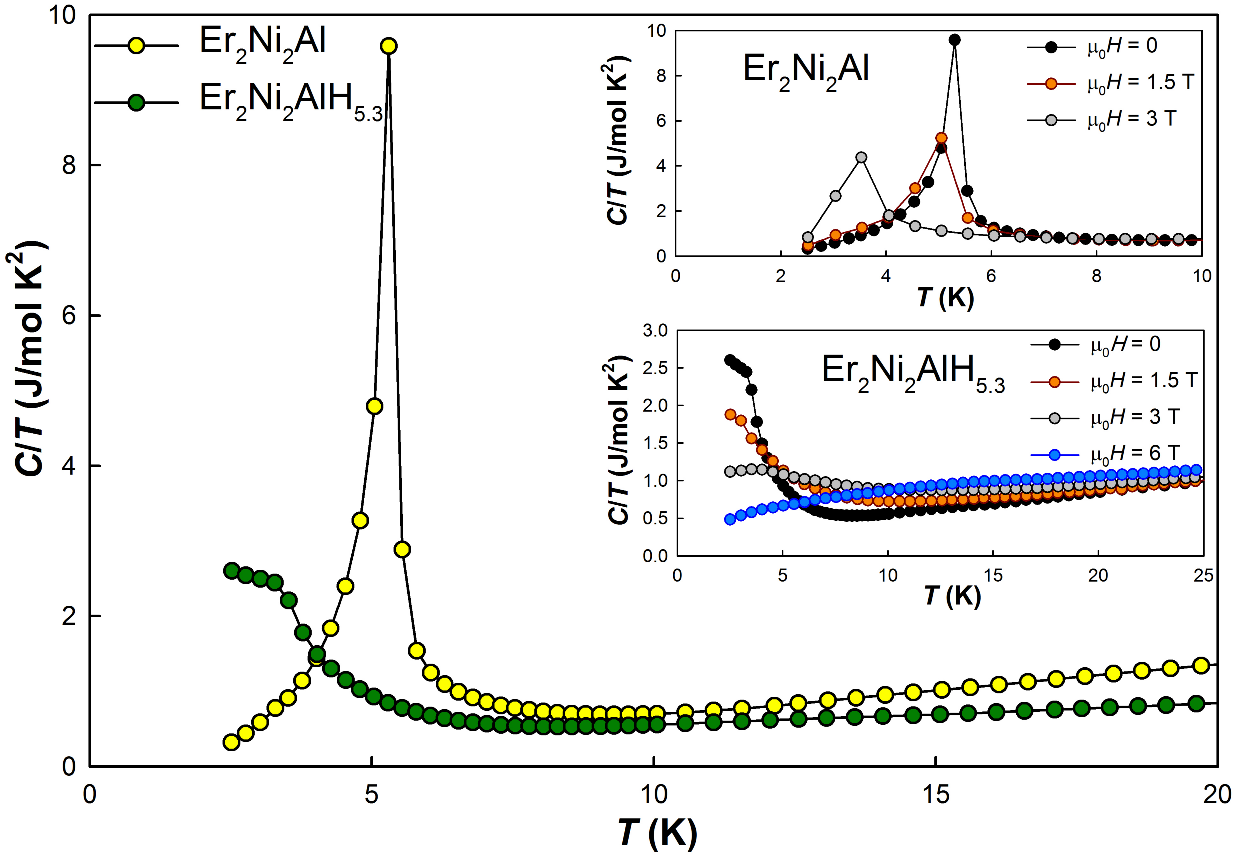


Fig. 3 Temperature dependence of the heat capacity of Er_2Ni_2Al and $Er_2Ni_2AlH_{5.3}$ measured without magnetic field. The insets show the temperature dependence of the heat capacity in magnetic fields.

The relatively low value of the ordering temperature prevented us from determining the Sommerfeld electronic heat capacity coefficient, which is proportional to the density of electronic states at the Fermi level. The application of a magnetic field consistently shifts the transition to lower temperatures, as expected for an antiferromagnet. No anomaly was observed on the temperature dependence of the heat capacity for $Er_2Ni_2AlH_{5.3}$. The upturn in C/T *vs.* T, which is suppressed by an applied magnetic field, is suggestive of magnetic ordering at still lower temperatures.

Discussion

The low-temperature data clearly establish that Er_2Ni_2Al is an antiferromagnet with $T_N = 5$ K. The obtained Curie-Weiss parameters differ somewhat from those obtained in the early 1980's [1]. The metamagnetic transition at 1-3 T indicates a change of the magnetic structure in relatively low fields.

In terms of crystal structure modifications, the hydrogenation leads to changes in the closest environment of the Er atoms. In the parent intermetallic the shortest Er–Er distance (3.32 Å) is found along the *c*-axis for pairs of atoms forming edges of the trigonal prisms surrounding the nickel atoms (marked as δ1 on Fig. 4). Such Er–Er pairs are separated by a distance equal to the lattice parameter *a* (δ2 = 4.15 Å), which is considerably larger than the distance δ3 (3.47 Å). Due to the strongly anisotropic lattice expansion occurring during the hydrogenation, the difference between the Er–Er distances is removed in the hydride: the distance δ1 increases up to 3.75 Å, while due to the lattice contraction in the *a*-direction, the distance δ2 becomes 3.84 Å. The distance δ3 is 3.81 Å, which results in a practically regular triangle of Er atoms as basis of the Er_3Ni tetrahedron, which is assumed to allocate the hydrogen atoms.

We suspect that the dramatic suppression of Er–Er exchange interactions in the hydride is mostly a consequence of hydrogen bonding. Such behavior is typical for most rare-earth intermetallics characterized by RKKY interactions [10]. The magnetic coupling that is achieved *via* the conduction electrons is strongly reduced because of the decrease of the conduction electron concentration due to the hydrogen uptake.

Conclusions

Er_2Ni_2Al, crystallizing with the orthorhombic W_2CoB_2 structure type, opens a new series of R_2T_2M compounds studied from the point of view of H absorption. As it is typical for pure 4*f* systems, the magnetic interactions are weakened after hydrogen absorption. While Er_2Ni_2Al is an antiferromagnet with $T_N = 5$ K, its hydride $Er_2Ni_2AlH_{5.3}$ does not order magnetically down to $T = 2$ K. The shape of the heat capacity curve indicates magnetic order at still lower temperatures. The most likely reason for the weakening of the magnetic interaction is the reduction of conducting electrons due to hydrogen bonding.

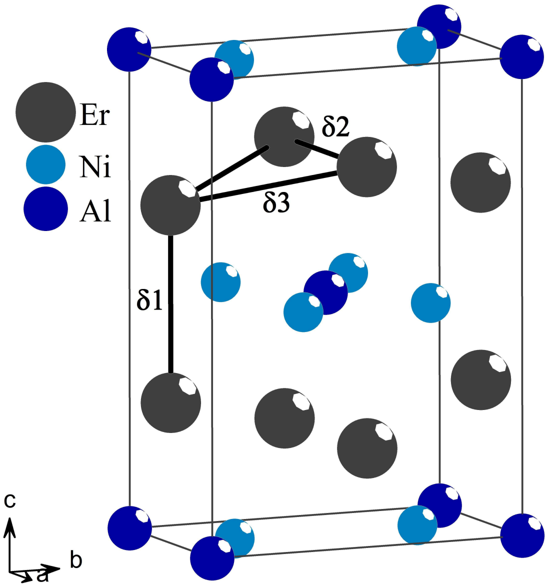


Fig. 4 Representation of the unit cell of Er_2Ni_2Al and $Er_2Ni_2AlH_{5.3}$. The Er–Er distances labeled δ1, δ2 and δ3 are discussed in the text.

Acknowledgements

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