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Large Magnetocaloric Effect in Nd_2Ni_2In

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Nd_2Ni_2In is an antiferromagnet ($T_N = 8$ K) with crystal structure equivalent to the Shastry-Sutherland lattice, possibly leading to the magnetic frustration. The AF coupling with moments in the basal plane can be driven by weak magnetic fields (< 0.2 T) into the c-axis ferromagnet. The situation leads to large changes of magnetic entropy in fields below 1 T, which makes Nd_2Ni_2In a candidate for magnetocaloric applications. The entropy change is 9.6 J/(kg K) in fields of 1 T.

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1. Introduction

Nd_2Ni_2In belongs to a large family of RE_2T_2X (RE = rare-earth or actinide, T = transition metal, X = p-metal) compounds crystallizing in the Mo_2FeB_2 structure type (space group $P4/mbm$) [1]. It is a layered structure with two types of basal-plane sheets, which alternate along the c-axis. The distinct layered character of the crystal structure may lead to large anisotropy in exchange coupling. The RE atoms form a triangular motif which, depending on the type of exchange interactions, can bring a geometrical frustration into the system, as it is equivalent to the 2-dimensional Shastry-Sutherland lattice arrangement [2].

Nd_2Ni_2In orders antiferromagnetically at $T_N = 8$ K [3]. In the present work we concentrate mainly on details of magnetic properties of Nd_2Ni_2In, studied on single-crystal, and on magnetocaloric properties.

2. Experimental

Nd_2Ni_2In polycrystal was prepared by arc melting of pure elements under Ar atmosphere. The button was remelted two times to ensure homogeneity. A single crystalline sample was prepared by the Czochralski technique in the tri-arc furnace. The quality of the single crystal was checked by XRD Laue technique, which was also used to orient the sample for further measurements.

Quantum Design PPMS equipment was used for magnetic studies and specific heat measurements. The specific heat has been so far measured on the polycrystalline sample only.

3. Results and discussion

Magnetization curve in the ordered state, obtained on the Nd_2Ni_2In polycrystal (Fig. 1) is not qualitatively different from a very narrow hysteresis loop of ferromagnet. Nevertheless, the neutron diffraction indicates an antiferromagnetic structure with Nd moments oriented mutually perpendicular along the direction of the < 110 > type, i.e. Nd moments in the basal plane. The data on single crystal (Fig. 2) reveal that the moments can be surprisingly easily canted to the c-direction in magnetic field of ≈ 0.2 T. The value of magnetization in such low magnetic fields corresponds to the value of magnetic moments obtained from neutron diffraction (2.49 μ_B/Nd at $T = 4$ K). We can therefore assume a ferromagnetic alignment of Nd moments in fields, along c.

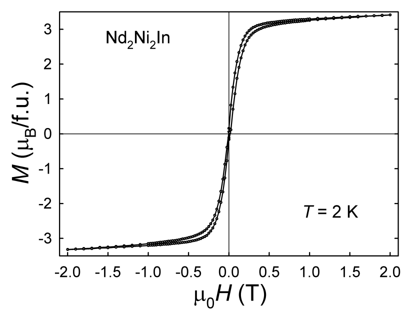

Fig. 1. Magnetization curve of the Nd_2Ni_2In polycrystal (randomly oriented powder) at $T = 2$ K.

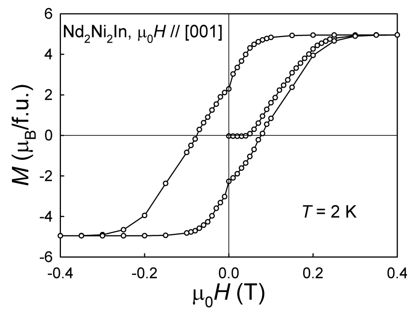

Fig. 2. Magnetization curve of Nd_2Ni_2In single crystal for field along the c-axis at $T = 2$ K.

Another peculiar feature is revealed with the T-dependence of magnetization. In low fields (< 0.2 T) the Néel temperature is marked by a sharp kink, not resembling a conventional magnetic phase transition (Fig. 3).

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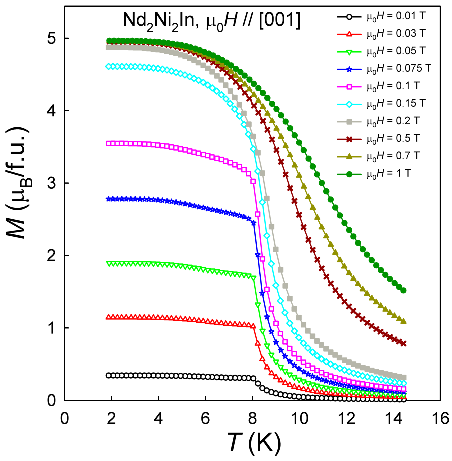

Fig. 3. Temperature dependence of magnetization of Nd_2Ni_2In, measured along the c-axis in various magnetic fields.

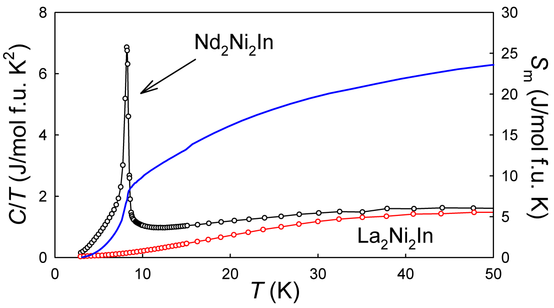

Fig. 4. Temperature dependence of the specific heat (in the C/T vs. T representation) for Nd_2Ni_2In as compared with La_2Ni_2In. The integrated difference curve gives the estimate of the magnetic entropy $S_m(T)$.

The peak in specific heat, related to magnetic ordering, does not form any λ-type anomaly (Fig. 4), expected for the 2^{nd} order magnetic phase transition (at least in the mean-field case). Instead we can see a sharp symmetric peak in the range 7.5–8.5 K. We can speculate about a weak first order transition. The peak tends to decrease in weak magnetic fields, and finally the sharp magnetic phase transition in Nd_2Ni_2In changes its character in magnetic field higher than 0.3 T. It starts to broaden and shifts to higher temperatures. The full magnetic entropy of Nd ion ($J = 9/2$) is $R\ln(10) = 19.14$ J/(mol K), which gives 38.28 J/(mol f.u. K) in our case. Determining the increment of magnetic entropy ΔS_m from 0 K to T we obtained only about 25% of the full value released up to T_N, whereas the increase continues to much higher temperatures and only slowly saturates when approaching $T = 50$ K. Relatively weak fields shift a lot of entropy by several Kelvin up (Fig. 5), testifying a certain magnetocaloric potential, with $\Delta S_m > 5$ J/(mol f.u. K) (9.6 J/(kg K)) in fields below 1 T. The fact that weak fields change the entropy considerably can be generally related to the magnetic frustration, making the magnetic

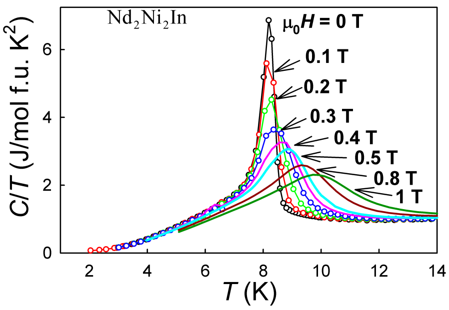

Fig. 5. Detail of the temperature dependence of the specific heat (in the C/T vs. T representation) for Nd_2Ni_2In in zero field and field variations of magnetic entropy $S_m(T)$ in $\mu_0 H = 0$ T (black line), 0.2 T (almost identical green line), 0.5 and 1 T (blue and red line, respectively).

order very sensitive. The obtained value is comparable with materials already considered for low temperature applications, but they can reach these values for much higher fields, e.g. $DyNi_5$ (15.4 J/(kg K) at $T_C = 12$ K and field change 0 − 5 T) [4].

4. Conclusions and future prospects

In conclusion, Nd_2Ni_2In shows a large ΔS_m, which indicates that such frustrated systems could be suitable magnetocaloric media, especially if similar effect is found for heavy rare-earths, which can develop higher magnetic entropy due to the higher multiplicity of magnetic moments in the paramagnetic state.

Future progress should reveal details of the magnetization processes in Nd_2Ni_2In. Apparently the states with Nd moments in the basal plane with non-collinear AF coupling in a square pattern on one side and ferromagnetic coupling of moments along c are nearly degenerate. c is actually the easy-magnetization direction in the paramagnetic state. So far it is not clear whether the moments are gradually canted by the field applied along c or there is a coexistence of domains with moments along c and in the ab-plane.

Acknowledgments

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