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Magnetic properties and specific heat of the Dy_3Ni intermetallic compound

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Abstract

We report measurements and analysis of the initial magnetic susceptibility and specific heat in polycrystalline Dy_3Ni and of magnetization processes in Dy_3Ni single crystals. The measured magnetic ordering temperature is $T_N = 38$ K and the spin-reorientation-transition and spin-freezing temperatures are $T_t \sim 23$–26 K and $T_{sf} = 53$ K, respectively. The field-induced magnetic transitions occur at 5.9, 8.3 and 6.4 T along the a, b and c axes, respectively, and strong magnetic anisotropy persists up to 13 T. The energy scales of the exchange interaction and field-induced magnetic structural deformation are comparable.

1. Introduction

The intermetallic compound Dy_3Ni crystallizes in the low-symmetry orthorhombic Fe_3C-type structure belonging to the *Pnma* space group, as do most other compounds with this stoichiometry. The first investigations of the magnetic properties of Dy_3Ni were made more than 30 years ago using pulsed magnetic fields of up to 16 T [1] and revealed a number of complex magnetic transitions. Since then, improved methods for growing single crystals and obtaining high magnetic fields have furthered interest in the magnetization processes in the family of R_3M compounds [2, 3]. However, there is still no clear understanding of which mechanisms are responsible for the magnetic behaviour in this compound. For example, there are significant variations in the values reported by different authors [3–5] for the magnetic ordering temperature, T_N, which cannot be explained solely by differences in sample purity or measurement methods.

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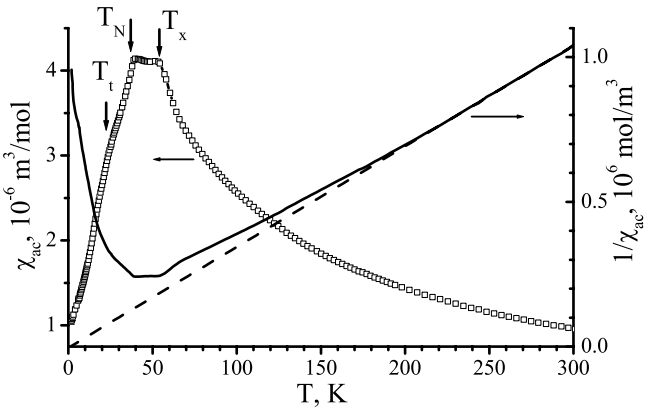

Figure 1. The initial magnetic susceptibility $\chi_{ac}(T)$ and inverse magnetic susceptibility $1/\chi_{ac}(T)$ of Dy_3Ni. The arrows show critical temperatures (see text for details).

The purpose of the present work is to provide a systematic analysis of the magnetic features of Dy_3Ni using measurements of the initial magnetic susceptibility and specific heat in polycrystalline samples, and to investigate magnetization processes in Dy_3Ni single crystals over a wide range of temperatures.

2. Experimental details

The Dy_3Ni samples were prepared by melting the constituent metals in an induction furnace in a purified argon atmosphere at 1.5 atm pressure, followed by slow cooling at $\sim$1–2 K s^{-1}. The purity of the dysprosium and nickel were 99.9 and 99.98%, respectively. X-ray measurements on the powdered samples showed a diffraction pattern consisting of lines that are characteristic of the Fe_3C-type structure, with no other phases found. The lattice parameters obtained for Dy_3Ni were $a = 0.686$ nm, $b = 0.950$ nm and $c = 0.629$ nm. Single-crystal elongated samples weighing 2–3 mg were extracted from the solidified ingots and then oriented by the conventional back Laue reflection method. It was found that disorder within the single crystals did not exceed 5°–7°.

The initial magnetic susceptibility was measured using an ac/dc susceptometer (from Oxford Instruments) in the temperature range 1.8–300 K in a 1 kHz magnetic field of 10^{-4} T. The specific heat measurements were performed using a Quantum Design PPMS Heat Capacity System in the temperature range 2–300 K. The magnetization measurements were carried out in the temperature range 1.5–130 K using a capacitance sensor magnetometer in static magnetic fields up to 13 T (the rate of the field increasing was 0.3 T min^{-1}). If the applied field direction and longitudinal axis of a sample did not coincide, the demagnetization factor was used.

3. Results and discussion

The temperature dependence of the initial magnetic susceptibility $\chi_{ac}(T)$ and specific heat $C_P(T)$ of polycrystalline Dy_3Ni are shown in figures 1 and 2, respectively. The temperatures of the observed anomalies are collected in table 1.

Comparison of the data obtained from specific heat and initial susceptibility measurements shows that the Néel temperature is $T_N = 38$ K and that the anomaly at $T_t \sim 23$–26 K corresponds to a spin reorientation transition. It is also worth noticing that the plateau-like

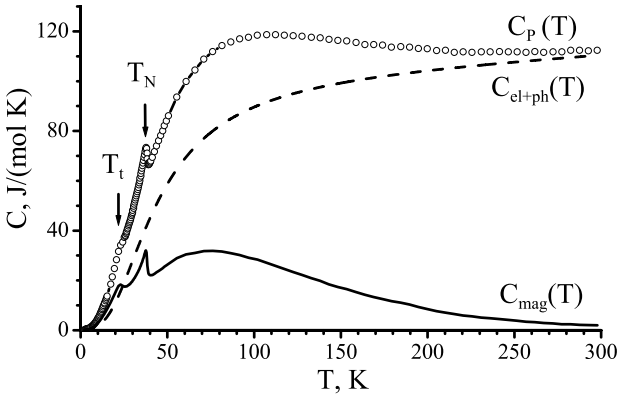

Figure 2. The calculated electron–phonon $C_{\mathrm{el+ph}}(T)$ and estimated magnetic $C_{\mathrm{mag}}(T)$ contributions to the experimentally obtained specific heat $C_P(T)$ of Dy_3Ni. The arrows show the temperatures of magnetic spin reorientation T_{t} and magnetic ordering T_{N}.

Table 1. The temperatures of the anomalies observed for Dy_3Ni by means of initial susceptibility and specific heat measurements.

	T_{t} (K)	T_{N} (K)	T_{sf} (K)
χ_{ac} (T)	∼26	38	53
C_P (T)	∼23	38	—

anomaly in the initial magnetic susceptibility, denoted as $T_{\mathrm{sf}} = 53$ K, was not observed in specific heat measurements, and that this temperature was found to be a reference temperature of the zero field cooled–field cooled (ZFC–FC) magnetic hysteresis [3]. There is evidence for short-range magnetic ordering remaining at temperatures significantly higher than T_{N}, including the deviation of the initial susceptibility from the Curie–Weiss law, the ZFC–FC hysteresis of magnetization, and the large anisotropy of magnetization in the paramagnetic phase. We propose that a spin-freezing phenomenon occurs in the temperature range between $T_{\mathrm{N}} = 38$ K and $T_{\mathrm{sf}} = 53$ K, and thus T_{sf} should be considered as the temperature of spin freezing.

It is well known that the specific heat for metals can be considered as the sum of independent electron, lattice (phonon) and magnetic contributions:

$$C_P(T) = C_{\mathrm{el}}(T) + C_{\mathrm{ph}}(T) + C_{\mathrm{mag}}(T). \tag{1}$$

The electron and phonon contributions to the specific heat can be calculated by the formula

$$C_{\mathrm{el+ph}}(T) = \gamma T + 9NR\left(\frac{T}{\Theta_{\mathrm{D}}}\right)^3 \int_0^{\Theta_{\mathrm{D}}/\mathrm{T}} \frac{x^4 \mathrm{e}^x}{(\mathrm{e}^x - 1)^2}\,\mathrm{d}x \tag{2}$$

where the first term represents an electron specific heat and the second term corresponds to a phonon contribution in accordance with Debye's model, γ is the Sommerfeld coefficient, Θ_{D} is the Debye temperature, $N = 4$ is the number of atoms per formula unit, and R is the molar gas constant.

To isolate the electron–phonon contribution from the total specific heat of magnetic Dy_3Ni, specific heat measurements were performed for an isostructural non-magnetic compound, Y_3Ni. It was found that, in the temperature range 2–300 K, the temperature dependence of the specific heat $C_P(T)$ of Y_3Ni can be fitted satisfactorily by formula (2), with Sommerfeld coefficient $\gamma = 41.5$ mJ mol^{-1} K^{-1} and Debye temperature $\Theta_{\mathrm{D}} = 234$ K.

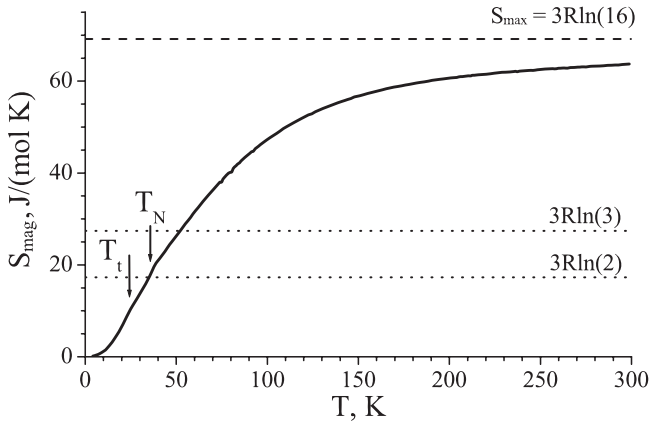

Figure 3. The magnetic entropy calculated for Dy_3Ni. The dashed line corresponds to the theoretical value $S_{max} = 3R\ln(2J + 1)$.

Since Dy^{3+} and Y^{3+} ions have an equal number of valence electrons, the γ parameter was assumed to be the same for Dy_3Ni and Y_3Ni. The Debye temperature for Dy_3Ni was evaluated using the method proposed in [6], taking into account the different atomic masses of Y_3Ni and Dy_3Ni, giving the result $\Theta_D = 179$ K. The electron–phonon contribution $C_{el+ph}(T)$ of Dy_3Ni was then calculated according to formula (2), and the magnetic contribution $C_{mag}(T)$ was estimated by subtracting the electron–phonon contribution from the total specific heat $C_P(T)$. The resulting electron–phonon $C_{el+ph}(T)$ and magnetic $C_{mag}(T)$ contributions are shown in figure 2.

In addition to the anomalies associated with the spin reorientation and Néel temperatures, the magnetic specific heat $C_{mag}(T)$ also exhibits a smooth wide maximum at $T \sim 75$ K, corresponding to a Schottky anomaly that is caused by crystal-field splitting of the Dy^{3+} ground-state level. A significant magnetic contribution to the specific heat remains up to temperatures as high as 250 K, which confirms our supposition of short-range magnetic ordering at temperatures significantly higher than the Néel temperature.

The magnetic part of the entropy $S_{mag}(T)$ was calculated using the standard formula:

$$S_{mag}(T) = \int_0^T \frac{C_{mag}(T)}{T}\,\mathrm{d}T \tag{3}$$

and the result is shown in figure 3. The analysis shows that the magnetic entropy at T_N is only slightly higher than $3R\ln(2)$, which means that only one Kramer's doublet takes part in the magnetic ordering.

As was found earlier, the magnetic entropy $S_{mag}(T)$ of R_3M compounds (where R = Er or Ho and M = Ni or Co) has a strong tendency to saturation, but does not approach the theoretical maximum value $S_{max} = 3R\ln(2J + 1)$ up to 300 K [7, 8]. This behaviour of the magnetic entropy can be explained by peculiarities in the ground-state level splitting by the crystal field when several doublets are separated from others by a substantial energy gap. Similar behaviour was observed for $DyCu_2$, which has a low-symmetry orthorhombic structure and for which the gap between the two highest and six other doublets was estimated to be about 100 K [9].

The magnetic entropy of Dy_3Ni also has a slight tendency to saturation at high temperatures and likewise does not reach the theoretical maximum value $S_{max} = 3R\ln(16)$ up to 300 K. However, for Dy_3Ni the deviation of the entropy from its theoretical maximum is significantly smaller than for Er_3Ni and Ho_3Ni. We suggest that the spectral splitting in Dy_3Ni is narrower

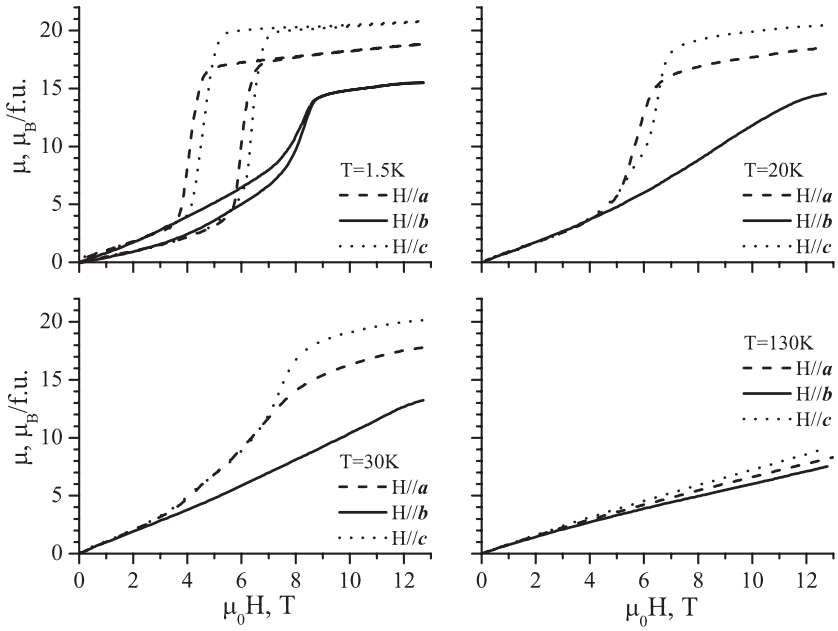

Figure 4. Selected isotherms of magnetization for Dy_3Ni single crystals.

than in Er_3Ni and Ho_3Ni, and hence the energy-level occupation varies more gradually and the magnetic entropy increases steadily.

Single-crystal magnetization measurements of Dy_3Ni were performed in static magnetic fields up to 13 T over a wide range of temperatures. Selected isotherms of the magnetization are shown in figure 4. At 1.5 K, the magnetization along the $\boldsymbol{a}$ and $\boldsymbol{c}$ crystallographic directions exhibits transitions in magnetic fields of 5.9 and 6.5 T, respectively, whereas the magnetization along the $\boldsymbol{b}$ axis increases gradually and is accompanied by a less pronounced jump at 8.3 T. Above the field-induced transitions, the magnetization increases linearly and a lack of saturation is observed for all crystallographic directions. At $T = 1.5$ K and $\mu_0 H = 13$ T, the magnetic moments are $\mu_{Dy_3Ni} = 18.8$, 15.6 and 20.8 μ_B/f.u. for magnetization along the $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$ axes, respectively. Therefore, assuming that nickel atoms do not carry any magnetic moment [10], one finds the magnetic moment per dysprosium atom to be $\mu_{Dy} = 6.3$, 5.2 and 6.9 μ_B for magnetization along the $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$ axes, respectively. These values are significantly lower than the magnetic moment in Dy_3Ni obtained by Mössbauer spectroscopy, $\mu_{Dy} = 10.0\ \mu_B$ per Dy^{3+} atom [3], which also corresponds to the magnetic moment of Dy^{3+} in pure metallic Dy at $T \to 0$ K [11]. Taking into account that magnetic anisotropy in Dy_3Ni persists up to high magnetic fields, we suggest that the magnetic structure of Dy_3Ni remains non-collinear even above the field-induced transitions.

By assuming that the magnetic moment of Dy^{3+} is close 10 μ_B and that nickel atoms do not carry ordered magnetic moments, one obtains an average deviation angle of $\theta \sim 51°$, 59° or 46° from the $\boldsymbol{a}$, $\boldsymbol{b}$, or $\boldsymbol{c}$ axes, respectively, at $\mu_0 H = 13$ T. On the other hand, neutron diffraction investigations have revealed that, at low temperatures, the magnetic moments of rare-earth atoms in Er_3Ni, Er_3Co and Dy_3Co are considerably smaller than the theoretical moments for the corresponding pure rare-earth metals [12, 13]. Hence the real deviation angles could be significantly smaller.

Table 2. The exchange interaction energy E_{ex}, anisotropy energy E_A, critical field H_{cr}, and the energy of initial magnetic structure deformation E_{def} at $T = 1.5$ K for Dy_3Ni.

E_{ex} (10^{-23} J)	E_A (10^{-23} J)	H_{cr} (T)	E_{def} (10^{-23} J)
	$\|a > 100$	$\|a$ 5.9	$\|a$ 54.7
74.5	$\|b > 95$	$\|b$ 8.3	$\|b$ 76.9
	$\|c > 115$	$\|c$ 6.4	$\|c$ 59.3

To analyze the magnetization processes in Dy_3Ni, we have estimated some typical energy scales. The total exchange energy can be evaluated from the magnetic ordering temperature:

$$E_{ex} = k_B T_N. \tag{4}$$

The energy of magnetic structure deformation E_{def} is related to the critical field H_{cr}:

$$E_{def} = g_J J \mu_B H_{cr} = 10\ \mu_B H_{cr}. \tag{5}$$

The energy of anisotropy can be derived from the magnetization-curve integral:

$$E_A = g_J J \mu_B H_A = 10\ \mu_B \int_0^\infty H\, \mathrm{d}M \tag{6}$$

where the magnetization M is given in μ_B, and $g_J = 4/3$ and $J = 15/2$ are the Landé factor and total angular momentum of the Dy atom, respectively.

For Dy_3Ni, the energy scale of the exchange interaction is comparable to that of the magnetic structure deformation (see table 2). However, since saturation is not observed, investigations in much stronger magnetic fields should be performed for a more precise estimation of the anisotropy energy.

The exact magnetic structure of Dy_3Ni is not known yet, but analysis of the field dependence of magnetization, and of the temperature dependence of the dc magnetic susceptibility in low magnetic fields [3], shows that, at $T = 4.2$ K in zero magnetic field, the projection of magnetic moments on all main crystallographic axes have antiferromagnetic ordering. It is also possible that the projection of the moment on the $\boldsymbol{b}$ axis is significantly smaller than those on the $\boldsymbol{a}$ and $\boldsymbol{c}$ axes, i.e. the moments are placed close to the ($\boldsymbol{ac}$) plane. We suggest that, to a certain extent, the magnetic structure of Dy_3Ni resembles that of isostructural Er_3Ni [12], except that the moments of Er_3Ni are placed in the ($\boldsymbol{ab}$) plane.

The application of an external magnetic field along the $\boldsymbol{a}$ or $\boldsymbol{c}$ axes leads to a two-step phase transition—a jump in magnetization is caused by a spin-flip-like reorientation of the magnetic moments in directions corresponding to local minima of the magnetic anisotropy and exchange energy, and then a further increase in magnetic field causes the magnetic moments to rotate in the direction of the applied field. The magnetization along the $\boldsymbol{b}$ axis has a different character—an increase in applied field leads to gradual rotation of the magnetic moments in the external field direction, and the magnetization passes through a number of metastable states. A subsequent decrease in the magnetic field leads to inverse rotation of the magnetic moments, but the magnetization passes through different metastable states, leading to an unusually shaped hysteresis.

Magnetic hysteresis was observed at low temperatures (below 10 K) for all main crystallographic directions. Increasing temperature leads to a very rapid reduction of the hysteresis; it is possible that the processes of field-induced magnetization and demagnetization are accompanied by the appearance of domain structure with narrow inter-phase boundaries of high intrinsic coercivity, as was supposed for the isostructural compound Dy_3Co [14].

Increasing temperature leads to smaller magnetization jumps, but the temperature dependence of the critical fields has a non-monotonic character. The field dependence

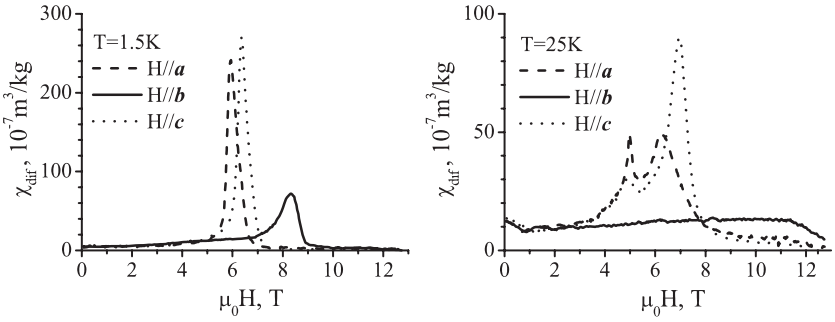

Figure 5. The field dependence of the differential susceptibility at $T = 1.5$ and 25 K.

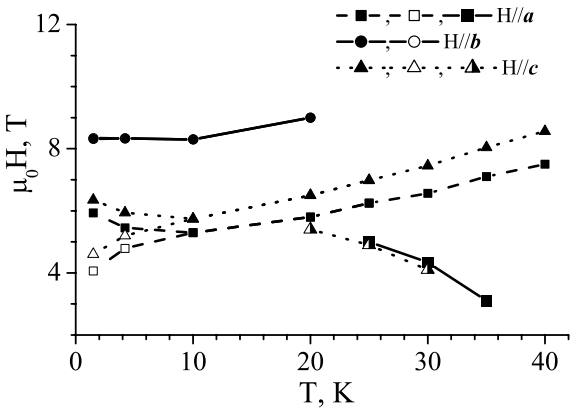

Figure 6. The temperature dependence of the critical fields of the induced phase transitions, constructed from magnetization isotherms along the main crystallographic directions. The filled and open symbols correspond to an increasing and decreasing field, respectively; semi-filled symbols correspond to additional peaks (see text for explanation).

of the differentiated susceptibility at $T = 1.5$ and 25 K is shown in figure 5 and the temperature dependence of the critical fields for the induced phase transitions (constructed from magnetization isotherms measured along the main crystallographic directions) is given in figure 6. The obtained phase diagram is in good accordance with previous data [3]. However, we have found a double anomaly of $\mu(H)$ in the temperature range 20–35 K for magnetization along the $\boldsymbol{a}$ and $\boldsymbol{b}$ axes.

We suggest that, in this temperature range (close to or above the spin-reorientation transition at T_t), the transformation of the magnetic structure is realized in several steps, i.e. the magnetic moments pass through several local energy minima when an external magnetic field is applied along the $\boldsymbol{a}$ or $\boldsymbol{c}$ axes. On the other hand, the existence of two non-equivalent positions for rare-earth ions in the low-symmetry Fe_3C-type crystal structure creates a situation where the effective magnetic fields acting on moments occupying the 4c and 8d positions are different. Thus, the magnetic structure of Dy_3Ni (and all other compounds of this stoichiometry) could be considered to consist of two sublattices. It is possible that, in the temperature range $T_t \leqslant T \leqslant T_N$, the phase transitions among magnetic moments occupying different crystallographic sites occur in different applied magnetic fields, leading to the observed double anomaly. To further test these hypotheses, more detailed investigations in this temperature range are needed.

4. Conclusions

The magnetic properties of the intermetallic compound Dy_3Ni have been investigated through measurements of the initial magnetic susceptibility and specific heat of polycrystalline Dy_3Ni and of the magnetization processes in Dy_3Ni single crystals. It was shown that the magnetic ordering temperature is $T_N = 38$ K, while the spin-reorientation-transition and spin-freezing temperatures were found to be $T_t \sim 23$–26 K and $T_{sf} = 53$ K, respectively.

The peculiarities of Dy_3Ni single-crystal magnetization processes are caused by the interplay of exchange interactions and strong anisotropy. The energy scale of the exchange interaction is comparable to that of magnetic structure deformation. The anisotropy of Dy_3Ni is caused not only by local ionic anisotropy, but also by its low-symmetry crystallographic structure. For more precise estimates of the anisotropy energy, investigations in much stronger magnetic fields should be performed.

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