Anomaly in the magnetocaloric effect in the intermetallic compound $DyAl_2$

P. J. von Ranke
IF, Universidade do Estado do Rio de Janeiro, DEQ, Rua São Francisco Xavier, 524, 20550-013, Rio de Janeiro, RJ, Brazil

I. G. de Oliveira
Universidade de Nova Iguacu, Av. Abilio Augusto Távora 2134, 26260, Rio de Janeiro, RJ, Brazil and Universidade do Grande Rio, Rua Prof. José de Souza Herdy 1160, Duque de Caxias, RJ, Brazil

A. P. Guimarães and X. A. da Silva
Centro Brasileiro de Pesquisas Físicas, Rua Dr. Xavier Sigaud 150, 22290-180, Rio de Janeiro, RJ, Brazil
(Received 25 January 1999)

It is well known that the intermetallic compound $DyAl_2$ is ferromagnetic and exhibits a change in the easy direction of magnetization from ⟨100⟩ to ⟨111⟩, for a critical applied magnetic field in the ⟨111⟩ direction. Using a simple model which includes the crystalline electric field and the exchange interaction we have theoretically investigated its magnetic entropy along the three main crystallographic directions. An anomalous behavior was theoretically predicted to exist in the magnetic entropy, which consists in the increase of entropy when the magnetic field is applied in the ⟨111⟩ direction. Comparisons between the theoretically predicted anomaly in $DyAl_2$ with the recent discovery of a magnetic anomaly in $PrNi_5$ are also presented.

INTRODUCTION

Magnetic refrigeration is based on the magnetocaloric effect, the ability of some magnetic materials to heat up when they are magnetized, and cool down when removed from the magnetic field in Ericsson thermodynamic cycle.[1] Improvements in the energy efficiency of magnetic refrigerators require working with substances having large magnetocaloric effect. The two thermodynamic quantities that characterize the magnetic caloric potential are ΔS_{mag} (the isothermal magnetic entropy change) and ΔT_{ad} (the adiabatic temperature change) which are observed upon changes in the external magnetic field.[2] Therefore improving in magnetic refrigeration, require investigations on the microscopic mechanisms that are responsible for increases in these two thermodynamic quantities, so a detailed understanding of the dependence of the ΔS_{mag} on the temperature and external magnetic field are useful.

Since Brown[3] described a practical near-room temperature magnetic refrigerator using magnetocaloric effects, and more recently, the discovery[4] of the giant magnetocaloric effect in $Gd_5(Si_2Ge_2)$, the interest in this research area has been considerably enhanced.[5,6] It was recently show[7] that $PrNi_5$ presents an anomalous increase of magnetic entropy in applied magnetic fields at low temperatures. This anomaly was completely understood and was associated with the crossing of the two lowest crystalline electrical field (CEF) levels.

In this paper, a similar anomalous behavior of the magnetic entropy in $DyAl_2$ is theoretically predicted to exist when this intermetallic compound [which crystallizes in the Laves phase structure ($C15$) and order ferromagneticaly at $T_c = 62\,\mathrm{K}$] is submitted to an external magnetic field pointed along the ⟨111⟩ direction. This yields an anomalous magnetocaloric effect in which the magnetic entropy of $DyAl_2$ increases (in a certain temperature region) when the compound is placed in an external magnetic field. This anomalous behavior is clearly observed in the negative part of the curve of $-\Delta S_{\mathrm{mag}}(T)$ vs temperature.

To carry out this investigation we have used a model Hamiltonian which takes into account the CEF in cubic symmetry, and the exchange interaction. The CEF was treated by the so-called point charge model, and the exchange interaction through the use of a molecular field approximation. In order to obtain a full description of CEF anisotropy effects on the dependence of the magnetization on magnetic field and temperature, we have used a two-dimensional and three-dimensional mean field theory when the magnetic field is applied along ⟨110⟩ and ⟨111⟩ direction, respectively. It was also possible to determine the critical magnetic field and the critical angle where the magnetization vector jumps from the ⟨100⟩ to the ⟨111⟩ direction. The results are in good agreement with the experimental data.

THEORY

The magnetism of $DyAl_2$ is described using a magnetic Hamiltonian that includes the CEF in cubic symmetry, and the Zeeman exchange interaction terms.

$$H = H_{\mathrm{CEF}} + H_{\mathrm{mag}}, \tag{1}$$

where

$$H_{\mathrm{CEF}} = B_4(O_4^0 + 5O_4^4) + B_6(O_0^6 - 21O_6^4) \tag{2}$$

and

$$H_{\mathrm{mag}} = -g\mu_B(\vec{B} + \lambda\vec{M})\cdot J. \tag{3}$$

Relation (2) is the single-ion CEF Hamiltonian where the O_n^m are the Stevens' equivalent operators.[8] The parameters

B_4 and B_6 determine the splitting of the $2J+1$ degenerate Hund's ground state (Dy has total angular momentum $J=15/2$). The CEF parameters used in this work are $B_4=-5.5\times10^{-5}$ meV and $B_6=-5.6\times10^{-7}$ meV obtained from the work of Purwins and Leson.[9]

Relation (3) is the single-ion Zeeman-exchange magnetic interaction, where g is the Landé factor, μ_B is the Bohr magneton, $\vec{B}$ is an external magnetic field, $\vec{J}$ is the total angular vector operator, and $\vec{M}=g\mu_B\langle\vec{J}\rangle$ is the magnetization. For $DyAl_2$, at low temperature and without external magnetic field, the easy magnetic direction is $\langle100\rangle$, which will be taken as the z-quantization direction. Under an external magnetic field applied in the $\langle111\rangle$ direction, the spontaneous magnetization will rotate from the $\langle100\rangle$ direction to the $\langle111\rangle$ direction, therefore, as suggested by Bak,[10] we must consider a three-dimensional mean field theoretical model. In this model the Zeeman-exchange term includes the three components of the magnetization vector and is written in the following way:

$$H_{\mathrm{mag}}=-g\mu_B(B_m^xJ^x+B_m^yJ^y+B_m^zJ^z), \tag{4}$$

where

$$B_m^x=B\cos(\alpha)+\lambda M^x, \tag{5}$$

$$B_m^y=B\cos(\beta)+\lambda M^y, \tag{6}$$

$$B_m^z=B\cos(\gamma)+\lambda M^z, \tag{7}$$

$$M^\eta=\left[\sum_n \exp\left(-\frac{e_n}{k_BT}\right)\right]^{-1}\sum_n \langle e_n|M^\eta|e_n\rangle\exp\left(-\frac{e_n}{k_BT}\right). \tag{8}$$

In Eq. (8), e_n and $|e_n\rangle$ are the eigenvalues and eigenvectors of the total Hamiltonian (1), $\cos(\alpha)$, $\cos(\beta)$, and $\cos(\gamma)$ are the direction cosines, and the other symbols have their usual meaning. The component of the magnetization in the direction of the applied magnetic field, M^η is obtained using the three mean field equations (5), (6), and (7), together with relation (8); in other words, the Hamiltonian (1) was diagonalized numerically and Eqs. (5)–(7) solved self-consistently, using an iteraction procedure for each given value of the magnetic field and temperature. The molar magnetic contribution to the entropy and heat capacity were obtained using the usual relations

$$S_{\mathrm{mag}}(B,T)=R\ln\left[\sum_n \exp\left(-\frac{e_n}{k_BT}\right)\right]+\frac{\langle E\rangle}{k_BT}, \tag{9}$$

where $\langle E\rangle$ is the mean energy and R is the universal gas constant.

RESULTS FOR $DyAl_2$

Using the two CEF parameters cited above and the exchange parameter[9] $\lambda=41.6\,\mathrm{T}^2/\mathrm{meV}$ for $DyAl_2$ and carrying out the procedure discussed above, we have obtained and plotted the magnetization vs magnetic field applied in the $\langle100\rangle$, $\langle110\rangle$, and $\langle111\rangle$ crystallographic main directions (calculated at $T=4.2$ K), see Fig. 1. The solid line and the symbols represent the theoretical and experimental results,[11] respectively.

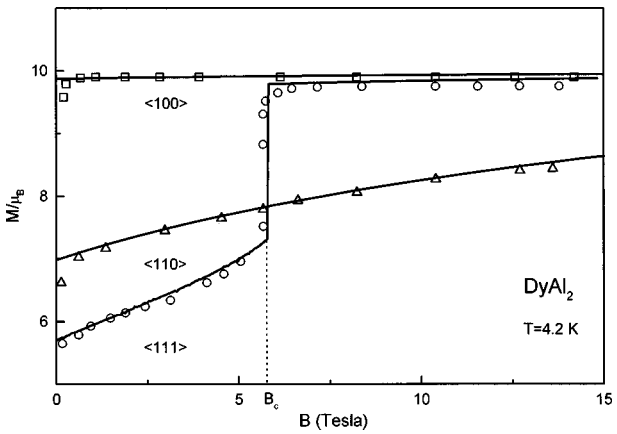

FIG. 1. Magnetization vs magnetic field applied in the $\langle100\rangle$, $\langle110\rangle$, and $\langle111\rangle$ directions for $DyAl_2$ calculated at $T=4.2$ K, using the exchange parameter and the CEF values from Ref. 9. The solid lines and the symbols ($\langle100\rangle$ squares, $\langle110\rangle$ triangles, and $\langle111\rangle$ circles) represent, respectively, the theoretical and experimental results.

The jump observed in Fig. 1 indicates the change in the easy magnetic direction from $\langle100\rangle$ to $\langle111\rangle$ that occurs, for $T=4.2$ K, at the critical field $B_c=5.8$ T. In Fig. 2 the angle $\Theta(B)$, formed by the magnetization vector and the initial $\langle100\rangle$ easy magnetization direction is displayed (see the inset of Fig. 2); this theoretical result was also calculated at $T=4.2$ K. Here we note that at the critical field, the angle where the jump of the magnetization vector occurs, $[\Theta(Bc)=12.6°]$, is predicted. There is a discontinuous behavior of the variation of the direction at the critical angle, from the previous value to $\Theta=54.73°$, which corresponds to the $\langle111\rangle$ direction in which the external magnetic field is applied. The magnetic field dependence of $\Theta(B)$ was determined using the magnetic field dependence of the three components of the total angular moment, i.e., $\tan(\Theta)=\sqrt{\langle J_y\rangle^2+\langle J_z\rangle^2}/\langle J_x\rangle$ (see the inset of Fig. 2).

In order to study the influence of the jump in magnetization on the magnetic entropy, we have used the relation (9),

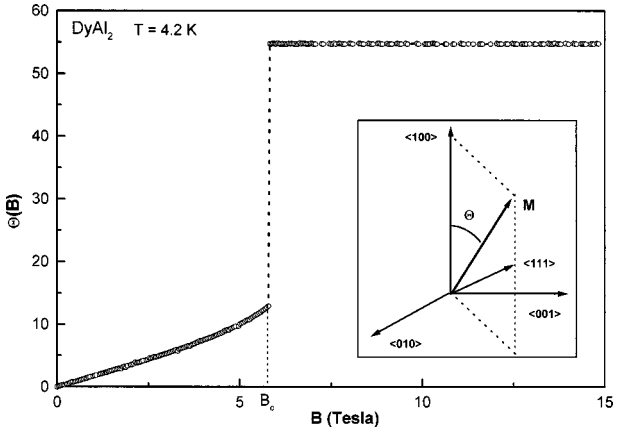

FIG. 2. The average thermodynamic value of angle vs magnetic field applied in the $\langle111\rangle$ direction calculated at $T=4.2$ K. The angle gives the direction of the magnetization vector in the $\langle100\rangle$-$\langle111\rangle$ plane, as shown in the inset.

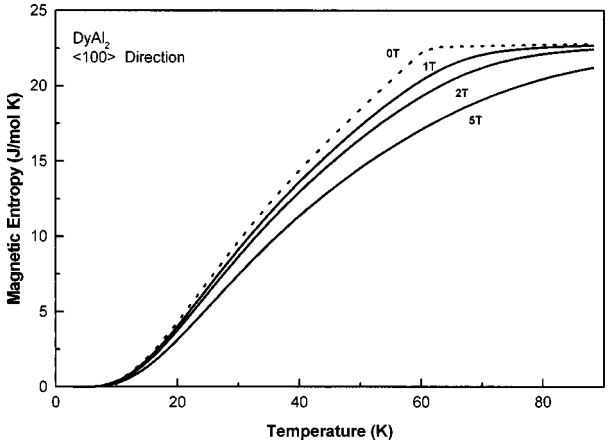

FIG. 3. Theoretical magnetic entropy vs temperature in $DyAl_2$ for different magnetic fields applied in the ⟨100⟩ direction. The dotted curve represents the magnetic entropy in zero magnetic field.

considering the external magnetic field applied in the three main directions. Figure 3 shows the magnetic entropies when the magnetic field is applied in the ⟨100⟩ direction ($B=0$, 1, 2, and 5 T). We can note the normal and expected behavior, i.e., the magnetic entropy decreases (in all temperature range) when the applied magnetic fields are increased. Figure 4 shows the magnetic entropies when the magnetic field is applied in the ⟨110⟩ direction for the same changes in magnetic fields as in Fig. 3. Note that, as in Fig. 3, the normal behavior in the entropy versus temperature and magnetic field is also observed. In contrast, for a magnetic field applied in the ⟨111⟩ direction (see Fig. 5) an anomalous and unexpected dependence of the entropy on applied magnetic field is theoretically predicted in the low-temperature region. This anomaly consists in the increase of the entropy, for a given temperature, when the magnetic field is increased. Two points must be made in relation to Fig. 5: (1) The temperature region where the anomaly appears becomes narrower when the applied field is increased and (2) The set of entropy curves for $B\neq 0$ T (full lines) have a normal behavior.

Figure 6 shows the change in magnetic entropy $-\Delta S_{\mathrm{mag}}(T)$ for applied magnetic fields changing from 0–1,

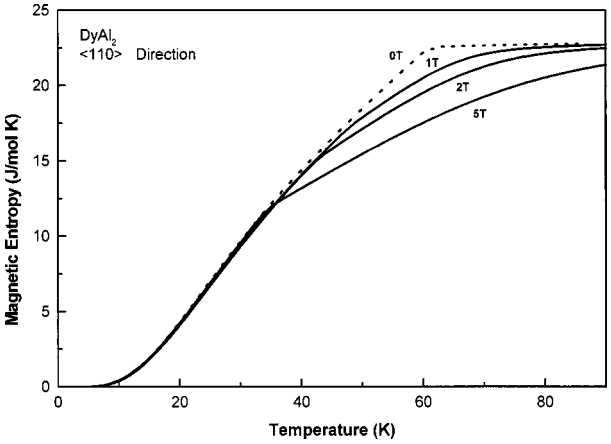

FIG. 4. Theoretical magnetic entropy vs temperature in $DyAl_2$ for different magnetic fields applied in the ⟨110⟩ direction. The dotted curve represents the magnetic entropy in zero magnetic field.

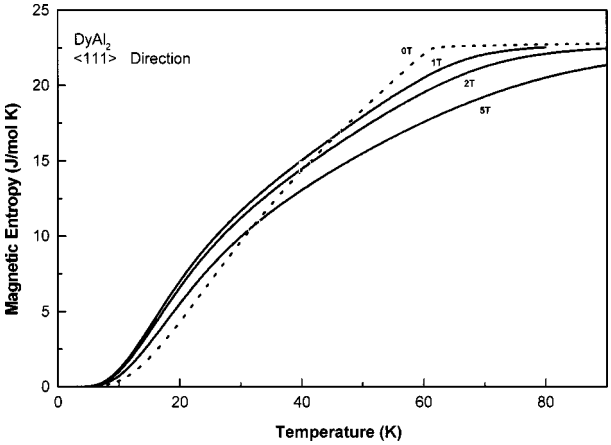

FIG. 5. Theoretical magnetic entropy vs temperature in $DyAl_2$ for different magnetic fields applied in the ⟨111⟩ direction. The dotted curve represents the magnetic entropy in zero magnetic field. The open squares mark the crossing points of the magnetic entropy, calculated both with applied fields and with zero magnetic field.

0–2, and 0–5 T. The negative region of $-\Delta S_{\mathrm{mag}}(T)$ evidences the anomaly in magnetic entropy for applied fields in the ⟨111⟩ direction.

DISCUSSION

The $DyAl_2$ compound presents a jump in the magnetization versus magnetic field (applied in the ⟨111⟩ direction) at $B_c=5.8$ T. This jump reflects the discontinuity, theoretically calculated, of the angle formed between the ⟨111⟩ direction and the magnetization vector direction. For $T=4.2$ K we obtain a change in the angle of $\Delta\Theta(B=B_c)\approx 42°$. This discontinuity is very large and can be described as a first order phase transition in the easy magnetic direction. The nature of the first order phase transition in systems of cubic symmetry (as it is the case of $DyAl_2$) has already been investigated within the framework of a three-state Potts model.[12]

We can see in Fig. 5 that the applied magnetic field in the ⟨111⟩ crystallographic direction yields an anomaly in the temperature region below the crossing point between the en-

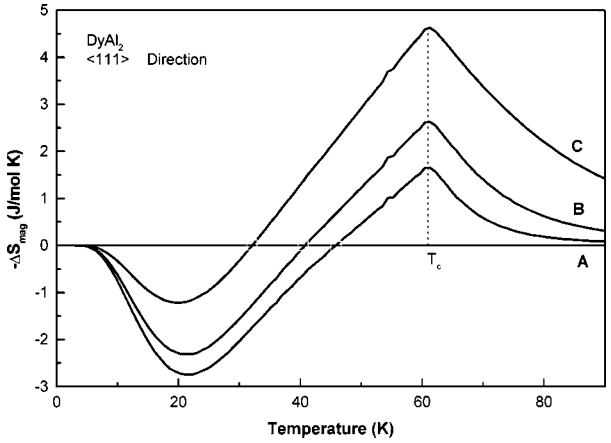

FIG. 6. Theoretical temperature dependence of the isothermal $-\Delta S_{\mathrm{mag}}$ in $DyAl_2$ for a magnetic field change in the ⟨111⟩ direction, from 0 to 1 T (curve A), 0 to 2 T (curve B), and 0 to 5 T (curve C).

tropy curve calculated at $B=0$ T (dotted curve) and the entropy curve for a given nonzero magnetic field. As the field increases the temperature in which the crossing occurs decrease; for $B=1$, 2, and 5 T we have the following temperatures: $T=45.8$, 40.7, and 32 K, respectively. These systematic theoretical results strongly suggest that, not only the magnetic field, but also the temperature plays a fundamental role in the change of the easy magnetic direction in $DyAl_2$.

The temperature dependence of the isothermal variation of magnetic entropy is obtained by subtracting the entropy calculated under an applied magnetic field from the magnetic entropy in zero magnetic field, i.e., $-\Delta S_{\mathrm{mag}}(T_i)=S(T_i,B=0)-S(T_i,B\neq 0)$. This physical quantity has practical importance since it gives the magnetocaloric potential[13] of the magnetic material (refrigerant). The magnetic entropy of the refrigerant is decreased to the extent of $\Delta S_{\mathrm{mag}}(T_i)$ and, therefore, the magnetic refrigerant loses $\Delta S_{\mathrm{mag}}(T_i)$ in the form of heat $Q_i \equiv T_i \Delta S_{\mathrm{mag}}(T_i)$ to the heat reservoir at temperature T_i. As shown in Fig. 6, the maximum magnetocaloric effect, for ferromagnetic systems is observed near or at the critical Curie temperature T_c, i.e., $Q_{\mathrm{max}} \equiv T_c \Delta S_{\mathrm{mag}}(T_c)$. As was well discussed by Dan'kov *et al.*,[14] this occurs because the two opposite tendencies (the ordering tendency due to exchange interaction of the magnetic moments, and the disordering tendency of the lattice thermal vibrations) are approximately balanced near T_c. Hence, the isothermal application of a magnetic field produces a much larger increase in the magnetization (i.e., an increase in the degree of magnetic order and, consequently, a decrease in magnetic entropy ΔS_{mag}) near the Curie point, rather than far away from T_c. In a normal magnetic refrigerant, ΔS_{mag} is significantly reduced below T_c, because the spontaneous magnetization is already close to saturation and cannot be increased substantially with an external magnetic field. But in the case of $DyAl_2$, investigated in this work, this argument cannot be applied any more, since, as shown in Fig. 6, below the square marks, the term $-\Delta S_{\mathrm{mag}}$ reaches negative values (increasing in module) instead of the normal behavior.

It has recently been theoretically discovered[7] (and also confirmed by experimentation) a similar anomaly in the paramagnetic $PrNi_5$ compound, which has its magnetic entropy increased, at low temperature (below $\sim$ 15 K), when the magnetic field is increased. The crucial difference is that in $DyAl_2$ all magnetic entropy curves (see Fig. 5), calculated with nonzero B, have a normal behavior, while the anomaly exists for the set of entropy curves in $PrNi_5$, even for nonzero B.

In the intermetallic compounds $DyAl_2$ and $PrNi_5$, the nature of the anomalous entropy is also different. For $DyAl_2$ its is associated with the first order transition discussed above, while for $PrNi_5$, the magnetic entropy anomaly comes from the crossing of the two lowest crystal electric field levels Γ_4 and Γ_1.

CONCLUSION

The anomaly in magnetic entropy changes (see Fig. 6) in $DyAl_2$ was theoretically investigated, using a Hamiltonian which takes into account the crystalline electric field and exchange interaction. An anomalous increase of magnetic entropy was predicted to occur in applied magnetic fields taken along the $\langle 111\rangle$ direction, compared with the entropy at zero magnetic field. This behavior is not usual in magnetic systems, since normally the effect of a magnetic field on magnetic systems is to align the magnetic moments parallel with the direction of field, and therefore, to reduce the magnetic entropy. When the applied magnetic field reaches the value of $B_c=5.8$ T it yields a first order directional magnetization transition with a large discontinuity of $\Delta\Theta(B=B_c)\approx 42°$.

The investigations of the nature of the magnetic phase transition in rare earth compounds have been the subject of our interest,[15–17] since it allows improvements in the new materials (refrigerant materials) used as active magnetic regenerators for magnetic refrigeration.[5]

ACKNOWLEDGMENT

One of us (P.J.v.R.) received financial support from the Universidade do Estado do Rio de Janeiro, which is gratefully acknowledged.

[1] T. Hashimoto, T. Kuzuhara, M. Sahashi, K. Inomata, A. Tomokiyo, and H. Yayama, J. Appl. Phys. **62**, 3873 (1987).
[2] M. E. Wood and W. H. Potter, Cryogenics **25**, 667 (1985).
[3] G. V. Brown, J. Appl. Phys. **47**, 3673 (1976).
[4] V. K. Pecharsky and K. A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997).
[5] K. A. Gschneidner, Jr. and V. K. Pecharsky, *Rare Earths: Science, Technology and Application III*, edited by R. C. Bautista, C. O. Bounds, T. W. Ellis, and B. T. Kilbourn (The Minerals, Metals and Materials Society, Warendale, 1997).
[6] P. J. von Ranke, V. K. Pecharsky, and K. A. Gschneidner, Jr., Phys. Rev. B **58**, 12 110 (1998).
[7] P. J. von Ranke, V. K. Pecharsky, K. A. Gschneidner, Jr., and B. J. Korte, Phys. Rev. B **58**, 14 436 (1998).
[8] K. W. H. Stevens, Proc. Phys. Soc. London, Sect. A **65**, 209 (1952).
[9] H. G. Purwins and A. Leson, Adv. Phys. **39**, 309 (1990).
[10] P. Bak, J. Phys. C **7**, 4097 (1974).
[11] B. Barbara, M. F. Rossignol, H. G. Purwins, and E. Walker, *Crystal Field Effects in Metals and Alloys*, edited by A. Furrer (Plenum, New York, 1977), p. 148.
[12] J. Cullen and E. Callen, Phys. Rev. B **30**, 181 (1984).
[13] M. E. Wood and W. H. Potter, Cryogenics **25**, 667 (1985).
[14] S. Yu. Dan'kov, A. M. Tishin, V. K. Pecharsky, and K. A. Gschneidner, Jr., Phys. Rev. B **57**, 3478 (1998).
[15] P. J. von Ranke and N. A. de Oliveira, Physica A **256**, 397 (1998).
[16] N. A. Oliveira, A. Caldas, and P. J. von Ranke, Physica B **253**, 158 (1998).
[17] P. J. von Ranke and N. A. de Oliveira, J. Appl. Phys. **83**, 6967 (1998).