ELSEVIER

Journal of Alloys and Compounds 218 (1995) 73–76

Journal of ALLOYS AND COMPOUNDS

Low temperature specific heat of DyBi and ErBi

H. Wada, H. Imai, M. Shiga

Department of Metal Science and Technology, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

Received 22 July 1994

Abstract

The low temperature specific heat of DyBi and ErBi was studied. It was found that DyBi shows a first-order phase transition at $T_N = 11$ K, while ErBi exhibits a double magnetic transition below 4 K. Analyses of the specific heat suggest that the ground state is a doublet for DyBi and a quartet for ErBi. The temperature dependence of the magnetic specific heat of ErBi is discussed in terms of the crystal field effects.

Keywords: Specific heat; Crystal fields

1. Introduction

In recent years much attention has been paid to rare earth compounds with large specific heat per unit volume at low temperatures as magnetic regenerative materials. Buschow et al. studied the heat capacities of several equiatomic rare earth compounds with a simple crystal structure [1]. They found that GdRh is superior to Pb as a cold regenerator.

Rare earth monopnictides have the f.c.c. NaCl-type structure. In spite of a simple crystal structure, the compounds with Ce show quite complex magnetic phase transitions [2]. On the other hand, the heavy rare earth compounds with As, Sb and Bi are type II antiferromagnets [3–5]. The Néel temperature T_N, which is 19–32 K for the Gd compounds [6], decreases on going from Gd to Er. While the specific heat has been studied for several arsenides and antimonides [7,8], no work has been reported on bismuthides. One advantage of monopnictides as large specific heat materials is their low Debye temperatures. The specific heat curve of non-magnetic LaBi was reported by Wallace et al. [9]. We found that this specific heat curve is well described by the Debye function with $\Theta_D = 165$ K in the temperature range below 40 K. By selecting appropriate rare earth elements, therefore, a large specific heat due to magnetic ordering is expected at low temperatures.

In this paper we report the low temperature specific heat of DyBi and ErBi.

2. Experiments

Polycrystalline samples of DyBi and ErBi were melted in sealed tantalum capsules by induction heating. The purity of the starting materials was 3N for the rare earth metals and 5N for Bi. X-Ray analyses showed that both samples have a single phase of NaCl-type structure. The low temperature specific heat was measured in a standard adiabatic calorimeter between 1.4 and 40 K.

3. Experimental results

Fig. 1 shows the specific heat curve of DyBi. A large anomaly was observed in the specific heat curve at $T_N = 10.9$ K. This Néel temperature is in agreement with the earlier report of $T_N = 13 \pm 1$ K [5]. As shown in the inset of Fig. 1, the antiferromagnetic transition is of first order. A similar transition was reported for DySb [7]. In order to separate the magnetic specific heat, the non-magnetic contribution has to be evaluated. Here the specific heat of LaBi was adopted for the non-magnetic part [9], which is shown in Fig. 1 by a full curve. The magnetic specific heat C_m of DyBi is shown in Fig. 2(a). It should be noted that C_m gradually increases with increasing temperature above T_N. This behaviour suggests that a Schottky-type specific heat associated with the crystal field becomes important above 40 K. Fig. 2(b) shows the temperature dependence of the magnetic entropy S_m of DyBi, which is evaluated

SSDI 0925-8388(94)01401-9

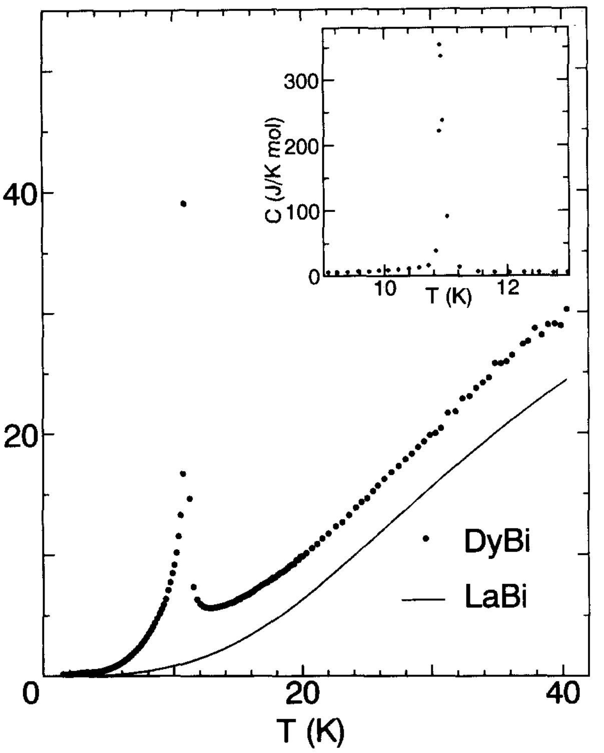

Fig. 1. Specific heat curve of DyBi. The full curve represents the specific heat of LaBi [9]. The inset shows the specific heat near T_N on an enlarged scale.

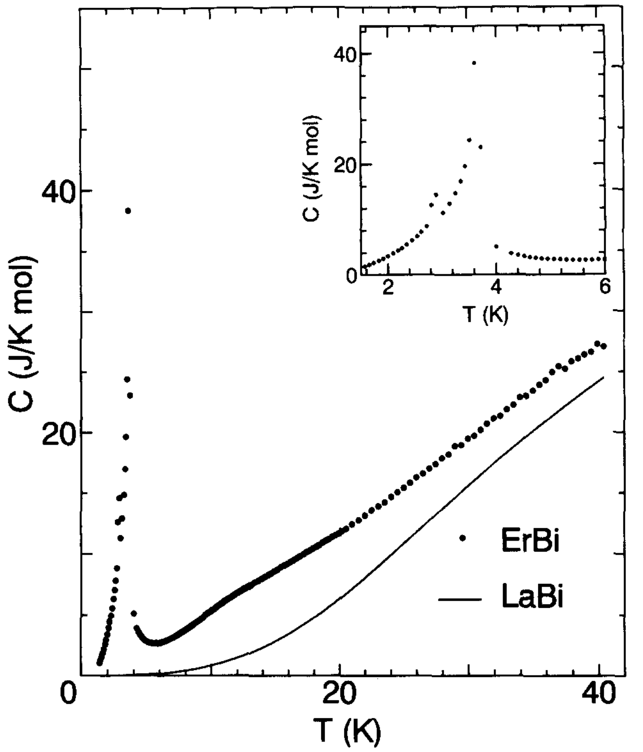

Fig. 3. Specific heat curve of ErBi. The full curve represents the specific heat of LaBi [9]. The inset shows the low temperature portion in detail.

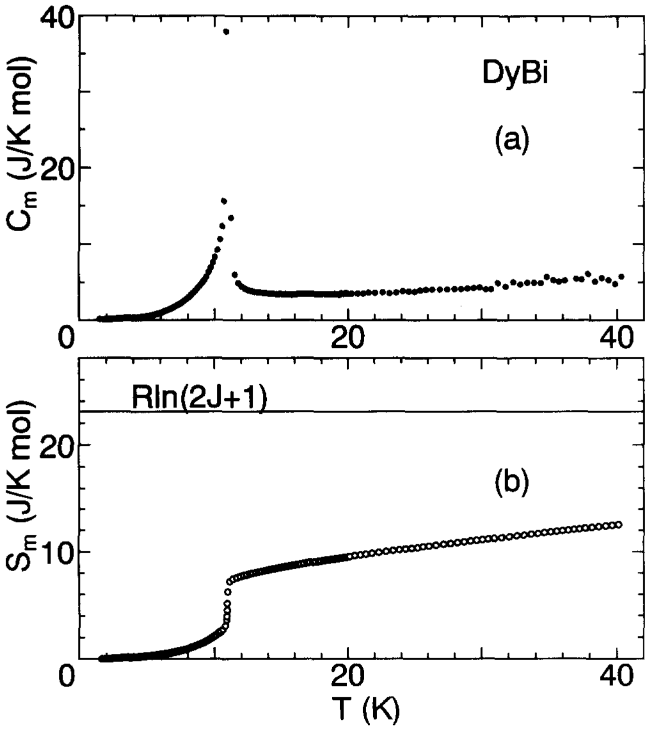

Fig. 2. (a) Magnetic specific heat of DyBi as a function of temperature. (b) Temperature dependence of magnetic entropy of DyBi. The full line is the entropy expected for Dy^{3+}, $R\ln(2J+1)$, with $J=15/2$.

by integrating C_m/T with respect to T. The magnetic entropy shows a jump at T_N, followed by a gradual increase with increasing temperature, reaching a value of 12 J K^{-1} mol^{-1} at 40 K. This value is much smaller than that expected for Dy^{3+}, $R\ln 16=23.1$ J K^{-1} mol^{-1}. This is consistent with the fact that C_m exists above 40 K owing to the crystal field effects.

The specific heat curve of ErBi is shown in Fig. 3. The specific heat anomaly around 3 K consists of two peaks, as shown in the inset of Fig. 3. This double transition is a common feature of the antiferromagnetic Er monopnictides [8]. By subtracting the specific heat of LaBi, C_m of ErBi was evaluated, which is shown in Fig. 4(a) as a function of temperature. Besides a sharp peak due to the antiferromagnetic transition, a broad peak is seen around 15 K which is a Schottky-type specific heat due to the crystal field. The temperature dependence of S_m of ErBi is shown in Fig. 4(b). The value of S_m at 40 K is 19 J K^{-1} mol^{-1}, which is about 80% of $R\ln(2J+1)$ for $J=15/2$.

4. Discussion

The present study has revealed that DyBi shows a first-order phase transition at T_N, while ErBi exhibits a double transition. These features were also observed

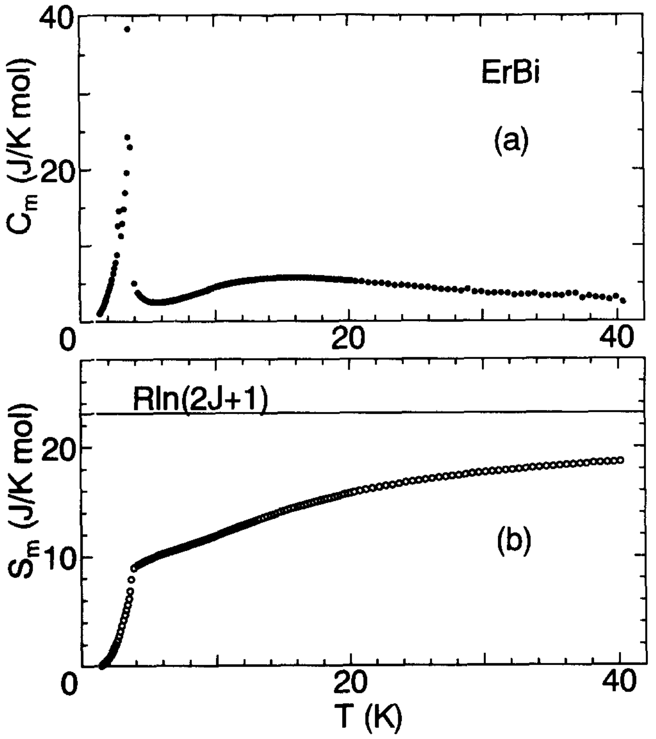

Fig. 4. (a) Magnetic specific heat of ErBi as a function of temperature. (b) Temperature dependence of magnetic entropy of ErBi. The full line is the entropy expected for Er^{3+}, $R\ln(2J+1)$, with $J=15/2$.

for the corresponding arsenides and antimonides [7,8].

In spite of the same quantum number $J=15/2$ for Dy and Er, it was found that S_m of DyBi is much smaller than that of ErBi in the whole temperature range that we studied. In the following we discuss the temperature dependence of S_m of these compounds in terms of the crystal field effects. In a cubic crystal field the 16-fold degeneracy for $J=15/2$ is lifted into two doublets and three quartets [10]. The ground state is either a doublet or a quartet. As described before, DyBi shows a first-order phase transition at T_N. The magnetic entropy around T_N is about 7.2 J K^{-1} mol^{-1} from Fig. 2. This entropy is explained by assuming that the paramagnetic ground state is a doublet. The exchange splitting suddenly disappears at T_N, which gives rise to the entropy change $R\ln 2=5.76$ J K^{-1} mol^{-1}. The small difference between S_m just above T_N and $R\ln 2$ can be reasonably ascribed to the magnetic entropy below T_N due to the temperature variation in the exchange splitting, which was demonstrated by neutron diffraction experiments [5]. A similar doublet ground state was also proposed for DySb by Bucher et al. [7]. The absence of a Schottky-type specific heat up to 40 K suggests that the energy separation due to the crystal field effects is large for DyBi. This is also supported by the temperature dependence of S_m, in which only 50% of $R\ln(2J+1)$ was acquired at 40 K for DyBi.

In the case of ErBi, S_m just above T_N is about 10 J K^{-1} mol^{-1}, being close to $R\ln 4=11.5$ J K^{-1} mol^{-1}. Therefore a quartet ground state is expected for ErBi. This compound shows a broad Schottky-type specific heat at around 15 K. The energy separation is smaller than that of DyBi. The observed S_m value at 40 K is 80% of $R\ln(2J+1)$, which also suggests that most of C_m due to the crystal field effects emerges up to 40 K. In order to discuss the crystal field effects more quantitatively, we have calculated the specific heat in the paramagnetic region. The cubic crystal field hamiltonian is given by [10]

$$H=W\left(x\frac{O_4}{F(4)}+(1-|x|)\frac{O_6}{F(6)}\right)$$

where W is a scale factor, O_4 and O_6 are the equivalent operators, $F(4)$ and $F(6)$ are the factors of matrix elements and x represents the relative importance of the fourth- and sixth-degree interactions. The specific heat was calculated by changing x and W. The best fits were obtained for two sets of the parameters x and W. These fits are shown in Figs. 5 and 6. In these figures the energy level schemes are also shown for each set of parameters. We cannot determine the energy level scheme uniquely by the specific heat alone. Nevertheless, it should be noted that both fits give a quartet ground state $\Gamma_8^{(3)}$, being consistent with the fact that S_m just above T_N is almost $R\ln 4$.

Finally, we refer to the possibility of applications of these materials. The Néel temperature of ErBi is below 4 K, which is too low for its application as a magnetic regenerator. Although T_N of DyBi lies within a suitable temperature range, the compounds shows a first-order

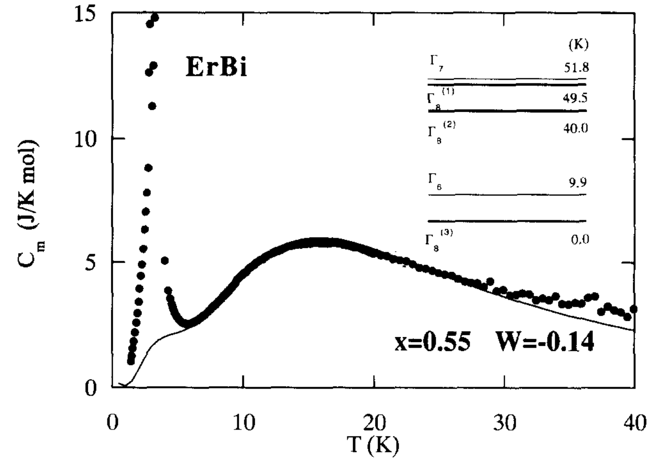

Fig. 5. Comparison of experimental and calculated magnetic specific heat of ErBi. The full curve represents the calculated results with $x=0.55$ and $W=-0.14$. The full circles are the experimental results. The energy level scheme is also shown.

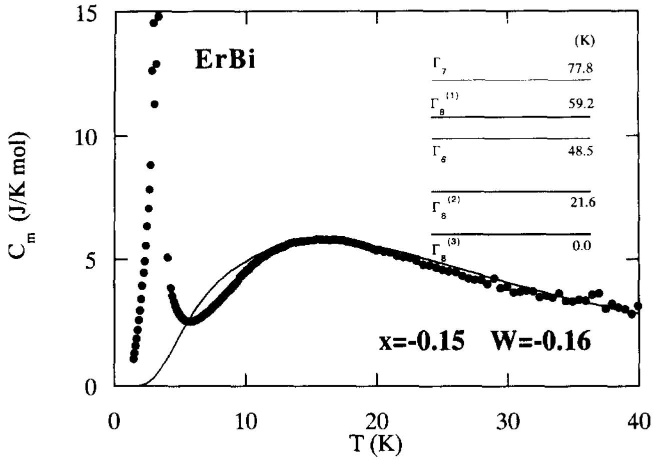

Fig. 6. Comparison of experimental and calculated magnetic specific heat of ErBi. The full curve represents the calculated results with $x = -0.15$ and $W = -0.16$. The full circles are the experimental results. The energy level scheme is also shown.

phase transition, which is not favourable for regenerative materials because they are required to exhibit a large specific heat in a wide temperature region below 15 K. Therefore more suitable materials are expected in the pseudobinary system $Dy_{1-x}Er_xBi$, the thermal properties of which are under investigation.

Acknowledgements

The authors are indebted to R. Iehara for his technical support. Thanks are also due to I. Arii for assistance in the experiments. This work is partially supported by a Grant-in-Aid for Developmental Scientific Research given by the Ministry of Education, Science and Culture of Japan.

References

[1] K.H.J. Buschow, J.F. Olijhoek and A.R. Miedema, *Cryogenics, 15* (1975) 261.

[2] J. Rossat-Mignod, P. Burlet, S. Quezel, J.M. Effantin, D. Delacote, H. Bartholin, O. Vogt and D. Ravot, *J. Magn. Magn. Mater., 31-34* (1983) 398.

[3] H.R. Child, M.K. Wilkinson, J.W. Cable, W.C. Koehler and E.O. Wollan, *Phys. Rev., 131* (1963) 922.

[4] T.R. McGuire, R.J. Gambino, S.J. Pickart and H.A. Alperin, *J. Appl. Phys., 40* (1969) 1009.

[5] N. Nereson and G. Arnold, *J. Appl. Phys., 42* (1971) 1625.

[6] G. Busch, *J. Appl. Phys., 38* (1967) 1386.

[7] E. Bucher, R.J. Birgeneau, J.P. Maita, G.P. Felcher and T.O. Brun, *Phys. Rev. Lett., 28* (1972) 746.

[8] V. Hovi, M. Lehtinen and R. Vuola, *Phys. Lett. A, 31* (1970) 451.

[9] W.E. Wallace, C. Deenadas, A.W. Thompson and R.S. Craig, *J. Phys. Chem. Solids, 32* (1971) 805.

[10] K.R. Lea, M.J.M. Leask and W.P. Wolf, *J. Phys. Chem. Solids, 23* (1962) 1381.