Heat-capacity studies of crystal-field effects in dilute $R\mathrm{Rh_4B_4}$ compounds

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Specific-heat data are presented for a number of compounds of the form $R_x\mathrm{Y}_{1-x}\mathrm{Rh_4B_4}$, where R (= Dy, Ho, Er, and Tm) is a rare-earth element and $x = 0.1$. Schottky anomalies arising from crystal-field splittings of the rare-earth ions are analyzed using crystal-field parameters recently determined for $\mathrm{ErRh_4B_4}$. Utilizing simple scaling arguments for the crystal-field parameters as the rare-earth ion is changed, a satisfactory explanation of the specific-heat data is obtained.

INTRODUCTION

The rare-earth rhodium borides $R\mathrm{Rh_4B_4}$, have provided an interesting system in which to study the interaction of superconductivity and long-range magnetic order. However, in many cases the interpretation of those studies has been complicated by the presence of unknown crystalline electric field (CEF) interactions. These CEF effects are observed in a number of ways, such as through the Schottky anomalies which they cause in the specific heat, the introduction of strong magnetic anisotropies, and by causing significant deviations from the trends normally expected for the magnetic transition temperatures. In order to investigate the problems of primary interest, it is frequently necessary to first evaluate the crystal-field interactions.

Heat-capacity measurements have traditionally played an important role in determining the crystal-field parameters. Schottky anomalies arising from a thermal average over the crystal-field—split state have been previously observed in concentrated $R\mathrm{Rh_4B_4}$ compounds.[1] However, many of the alloys show magnetic ordering which masks the simple crystal-field effects. In such cases, the study of dilute alloys such as $\mathrm{Y}_{1-x}R_x\mathrm{Rh_4B_4}$ is useful in order to reduce the magnetic transition temperature without significantly altering the crystal fields. In this paper we report heat-capacity measurements on $\mathrm{Y}_{0.9}R_{0.1}\mathrm{Rh_4B_4}$ for $R =$ Dy, Ho, Er, Tm, and Lu, and compare these results with a recent crystal-field model for these materials.

DATA ANALYSIS

The low-temperature heat capacity for $\mathrm{Y}_{0.9}R_{0.1}\mathrm{Rh_4B_4}$ with $R =$ Dy, Ho, Er, Tm, and Lu is shown in Fig. 1. Superconducting transitions are clearly observed for all the compounds shown. In order to derive the CEF contribution to the heat

capacity, the lattice and electronic terms have been subtracted using $\mathrm{Y}_{0.9}\mathrm{Lu}_{0.1}\mathrm{Rh_4B_4}$ as a background material. Lu is nonmagnetic, and is expected to provide a good approximation to the lattice heat capacity, since it has an atomic weight which is only slightly heavier than the other rare earths. This difference will cause some systematic error, since the phonon modes involving the Lu atoms will occur at lower energies, assuming the force constants do not change radically on going across the rare-earth series. It is possible to make estimates of this error based on simple models, and these are included in the total "error bars" shown in Figs. 3—5. This type of error will depend on temperature, and will be most important for rare earths such as Ho and Tm, which have Schottky anomalies occurring at temperatures (30—40 K) where the lattice contribution to the heat capacity is dominant.

For dilute alloys, the magnitude of the specific-heat jump at T_c is not insignificant compared to the Schottky anomalies, in contrast with the concentrated systems. While the magnitude of the jumps at T_c are similar for the different R's, the T_c values vary sufficiently to cause problems with the background subtraction very near the transition. For this reason, it is useful to subtract from the raw data below T_c an entropy-constrained function which represents the superconducting heat capacity of each rare-earth compound $\mathrm{Y}_{0.9}R_{0.1}\mathrm{Rh_4B_4}$. The function was based on the nonmagnetic heat capacity of $\mathrm{YRh_4B_4}$, and was scaled according to the law of corresponding states by the T_c of each compound.

CRYSTAL-FIELD CALCULATIONS

The crystal-field Hamiltonian appropriate for the $\overline{4}2m$ symmetry of the rare-earth ions in this case is

$$H_{\mathrm{CF}} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^4 O_6^4 , \quad (1)$$
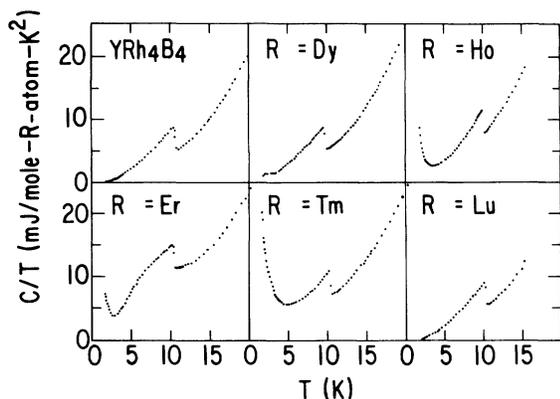
where the O_n^m are Stevens operators. The B_n^m are

FIG. 1. Heat capacity of $Y_{0.9}R_{0.1}Rh_4B_4$, with R=Dy, Ho, Er, and Lu.

FIG. 3. Specific-heat data (solid points) and calculated values (solid line) for $Y_{0.9}Er_{0.1}Rh_4B_4$. Error bars include estimates for both random and systematic error.

commonly written as

$$B_n^m = A_n^m \langle r^n \rangle \alpha_n , \qquad (2)$$

where the $\langle r^n \rangle$ are radial integrals determined from Hartree-Fock calculations, and the α_n are Stevens factors.[2] The A_n^m are often assumed to be independent of the particular rare-earth ion in an isostructural series of compounds, and we will make that assumption in the following. In that case, the variation of the crystal-field parameters as the rare-earth ion is changed is determined solely by $\langle r^m \rangle$ and α_n, which are all known quantities.
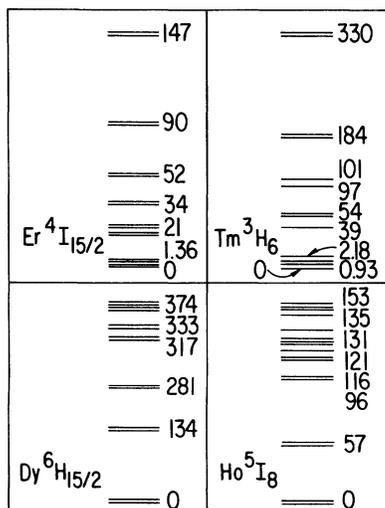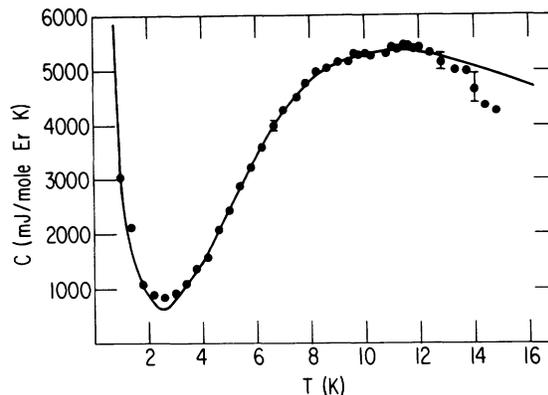
The five parameters B_n^m of Eq. (1) have been re-

FIG. 2. Crystal-field levels for RRh$_4$B$_4$ compounds, calculated using the parameters of Table I.

cently determined[3] for ErRh$_4$B$_4$ using the results of a Mössbauer effect experiment which provided a value for B_2^0, and single-crystal magnetization used to determine the other parameters. Final parameter refinement was carried out using both the magnetization data and the specific-heat data for $Y_{0.9}Er_{0.1}Rh_4B_4$ discussed below. Values of B_n^m for other compounds were determined using Eq. (2) and the assumption of constant A_n^m. This procedure has provided a substantial consolidation of many of the physical property measurements in these compounds.

The crystal-field parameters obtained as described above are given in Table I for R=Dy, Ho, Er, and Tm, and the crystal-field energy levels E_i obtained through Eq. (1) are shown in Fig. 2. Details of the wave functions so obtained will be discussed separately with regard to the magnetic properties.[4] For present purposes, the Schottky anomalies in the specific heat can be calculated according to

$$C_{\text{Schottky}} = \frac{R}{T^2} (\langle E_i^2 \rangle - \langle E_i \rangle^2) ,$$

where enclosure by the angular brackets denotes a thermal average over all levels. Such calculations are compared with the data in the next section. It should be emphasized that the parameters of Table I have been determined from experimental data only for the Er compound. Calculations for other members of the series are done with no further empirical adjustment and no assumptions other than that expressed in Eq. (2).

DISCUSSION

The specific-heat data obtained for $Y_{0.9}Er_{0.1}Rh_4B_4$ are shown in Fig. 3. A comparison

TABLE I. Crystal-field parameters for $R\mathrm{Rh}_4\mathrm{B}_4$ compounds (measured in K/a.u.).

	B_2^0	B_4^0 (10^{-3})	B_4^4 (10^{-3})	B_6^0 (10^{-6})	B_6^4 (10^{-6})
$\mathrm{DyRh}_4\mathrm{B}_4$	-2.10	-2.03	9.78	-0.89	-2.26
$\mathrm{HoRh}_4\mathrm{B}_4$	-0.70	-1.06	5.03	0.98	2.49
$\mathrm{ErRh}_4\mathrm{B}_4$	0.77	1.30	-6.19	-1.39	-3.52
$\mathrm{TmRh}_4\mathrm{B}_4$	2.97	4.75	-21.76	3.45	8.75

with the data for the concentrated $\mathrm{ErRh}_4\mathrm{B}_4$ has been previously given.[5] As stated above, these data have been used in finalizing the parameters, and the agreement with experiment between data and calculation is seen to be excellent. This material provides the best test of crystal fields in the series because the Schottky anomaly is the most pronounced in comparison to $\mathrm{LuRh}_4\mathrm{B}_4$ or $\mathrm{YRh}_4\mathrm{B}_4$ (see Fig. 1). The specific heat is characterized by a low-temperature upturn due to the low-lying doublets separated by 1.4 K, and by a broad maximum peaking at 11 K due to the other levels. The observation of the low-temperature feature is in agreement with magnetic entropy measurements, which require four low-lying states.[6] Inclusion of level splitting from exchange effects on the low-lying states should adequately explain the unusual features of the specific heat of $\mathrm{ErRh}_4\mathrm{B}_4$ in the vicinity of its ferromagnetic transition. This has been demonstrated in a simple model by Woolf and Soukoulis.[7]

Specific-heat data for $\mathrm{Y}_{0.9}\mathrm{Ho}_{0.1}\mathrm{Rh}_4\mathrm{B}_4$ are shown in Fig. 4, along with the data[6] for $\mathrm{HoRh}_4\mathrm{B}_4$ taken above the magnetic transition temperature. In this case, the low-temperature upturn does not arise from low-lying crystal-field levels, but from a nuclear Schottky effect due to magnetic splitting of the nuclear energy levels. This was also seen in

$\mathrm{HoRh}_4\mathrm{B}_4$, and is expected for a magnetically ordered system. Its occurrence in the dilute sample, where no magnetic ordering occurs, is unusual, but has a simple explanation. Wave functions corresponding to the ground-state crystal-field doublet calculated from the parameters in Table I show that the state has angular-momentum values $J_z = \pm J = \pm 8$. Ordinary electronic spin-relaxation processes produce transitions only for $\Delta J_z = \pm 1$. The only mechanism allowing spin relaxation for this doublet involves very-high-order phonon processes, which occur with very low probability. Hence the ground-state doublet is virtually static, with each component of the doublet producing a large hyperfine field at the Ho nucleus and no time-dependent averaging of this field occurring. In the calculated curve of Fig. 4 the nuclear Schottky anomaly has been taken to be identical with Ho metal,[8] and this agrees with the data. This in turn implies an electronic magnetic moment near the free-ion value as previously noted.[6] Such a moment is consistent with the ground state described above.

The crystal-field Schottky anomaly for the Ho compound consists of a broad maximum peaking at 25 K. As one sees, the calculated peak occurs at a slightly higher temperature. In view of the subtraction difficulties inherent in obtaining these data, and
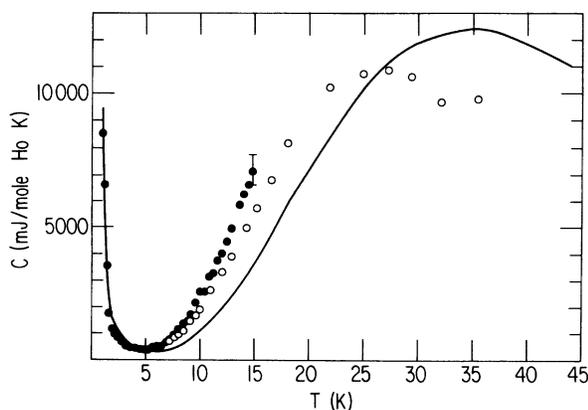

FIG. 4. Specific-heat data for $\mathrm{Y}_{0.9}\mathrm{Ho}_{0.1}\mathrm{Rh}_4\mathrm{B}_4$ (solid circles) and $\mathrm{HoRh}_4\mathrm{B}_4$ (open circles, Ref. 6), with calculated values (solid line). Error bars include estimates of both random and systematic errors.
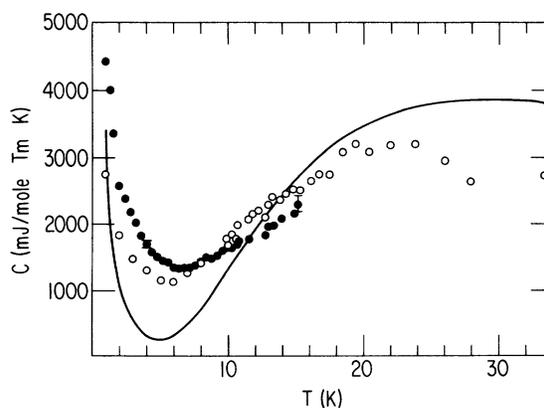

FIG. 5. Specific-heat data for $\mathrm{Y}_{0.9}\mathrm{Tm}_{0.1}\mathrm{Rh}_4\mathrm{B}_4$ (solid circles) and $\mathrm{TmRh}_4\mathrm{B}_4$ (open circles, Ref. 1), with calculated values (solid line). Error bars include estimates of both random and systematic errors.

the restrictive assumptions associated with Eq. (2), the agreement with experiment is very good.

Data for $Y_{0.9}Tm_{0.1}Rh_4B_4$ are shown in Fig. 5, along with previous results for $TmRh_4B_4$.[1] From Fig. 2, one sees that there are four low-lying states within about 2 K of one another, and these cause the low-temperature increase seen in the specific heat. The remaining levels give rise to a very broad maximum peaking at about 30 K. The calculated curve is in generally good agreement with the data. In view of the several levels near the ground state, it is clear that small variations in the crystal-field parameters will cause significant changes in the calculated specific heat in that region. However, because five parameters are involved in the calculation and no single-crystal magnetization data exist, no attempts have been made to further refine the parameters at this time.

Data obtained for $Y_{0.9}Dy_{0.1}Rh_4B_4$ show no significant crystal-field effects up to 15 K, in agreement with previous $DyRh_4B_4$ results.[6] The calculated specific heat gives a maximum peaking at 85 K, consistent with the data.

CONCLUSIONS

Data have been presented for the specific heat of $Y_{0.9}R_{0.1}Rh_4B_4$ compounds with $R=Dy$, Ho, Er, and Tm, and compared with calculations based on a crystal-field model. In that calculation, the crystal-field parameters A_n^m have been fixed for Er, and then assumed to be constant for the other compounds. Although no additional adjustable parameters are present, one sees that good agreement is obtained between data and calculations. This provides a substantial verification of the validity of the crystal-field parameters. In turn, this allows the inclusion of crystal-field effects in other phenomena and the clarification of problems which cannot be resolved by invoking crystal-field effects.

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[1]L. D. Woolf, D. C. Johnston, H. B. MacKay, R. W. McCallum, and M. B. Maple, J. Low. Temp. Phys. 35, 651 (1979); H. B. MacKay, L. D. Woolf, M. B. Maple, and D. C. Johnston, ibid. 41, 639 (1980); H. C. Hamaker, H. B. MacKay, M. S. Torikachvili, L. D. Woolf, M. B. Maple, W. Odoni, and H. R. Ott, ibid. 44, 553 (1981); L. D. Woolf, Ph.D. thesis, University of California San Diego, 1980 (unpublished).

[2]Values of these parameters for rare-earth ions are tabulated by P. Fulde, in Physics and Chemistry of Rare-earths, edited by K. A. Gschneider, Jr. and L. Eyring (North-Holland, 1979), Vol. 2, p. 300.

[3]B. D. Dunlap and D. G. Niarchos, Solid State Commun. 44, 1577 (1982).

[4]B. D. Dunlap and D. G. Niarchos (unpublished).

[5]H. B. Radousky, G. S. Knapp, J. S. Kouvel, T. E. Klippert, and J. W. Downey, in Ternary Superconductors, edited by G. K. Shenoy, B. D. Dunlap, and F. Y. Fradin (North-Holland, Amsterdam, 1981), p. 151—154.

[6]H. R. Ott, L. D. Woolf, M. B. Maple, and D. C. Johnston, J. Low Temp. Phys. 39, 383 (1980).

[7]L. D. Woolf and C. M. Soukoulis, Bull. Am. Phys. Soc. 27, 246 (1982); L. D. Woolf, Phys. Lett. 93A, 419 (1983).

[8]O. V. Lounasmaa, Phys. Rev. 128, 1136 (1962).