SPECIFIC HEAT OF $RBa_2Cu_3O_{7-x}$ AND $RBaSrCu_3O_{7-x}$ COMPOUNDS (R = Sm, Dy, Er)

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The low-temperature specific-heat $C(T)$ data of high-T_c superconductors $RBa_2Cu_3O_{7-x}$($R123O_{7-x}$) were reviewed. A discussion of the $C(T)$ data obtained on single-crystalline samples of $Er123O_{7-x}$ and $Sm123O_{7-x}$ compounds in applied magnetic fields for better evaluation of the crystal-electric-field parameters is given. The $C(T)$ measurements of Sr-substituted compounds $RBaSrCu_3O_7$ revealed the λ-type of peak related to the antiferromagnetic order at 1.2 K and 0.6 K respectively for Dy- and Er-compounds. The magnetic singlet ground state in these compounds is produced by weak exchange interactions of -0.05 T/μ_B and -0.035 T/μ_B, respectively. For Nd- and Sm-compounds, only a broad anomaly around 0.6 K was observed which is well fitted with a Schottky-type anomaly with an energy splitting of 1.4 K.

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1. Introduction

One of the interesting features of the high-T_c superconductors $RBa_2Cu_3O_{7-x}$ ($R123O_{7-x}$) (R denotes rare earth, $T_c \approx 90$ K) is the coexistence of the magnetism and superconductivity. It turned out that the low-temperature magnetic properties of these compounds are well described by crystal-electric-field (CEF) approach applied to the f^n configurations of the R^{3+} ions [1–5]. The extensive inelastic-neutron-scattering (INS) studies have revealed numbers of CEF transitions in these compounds and the sets of CEF parameters describing the ground

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state (GS) of the R^{3+} ions have been evaluated [1–5]. Recently, the specific-heat measurements have been reported for Nd-, Sm- and Dy123O_{7-x} compounds (poly-crystalline samples) over the whole oxygen range (i.e. $x = 0 \div 1$) [6]. The authors attempt to explain the results in the frame of the magnetic cluster model. However, the low-temperature specific-heat measurements performed on single-crystalline samples, especially in applied magnetic field, supply direct evidence for anisotropy of magnetic properties which can be well described within the CEF model. They allow for further refinement of CEF parameters obtained from INS studies [7, 8]. The Sr-substituted compounds RBaSrCu$_3$O$_{7-x}$ are known to belong to R123O$_{7-x}$ family with T_c between 54 and 86 K [9]. With the Sr substitution, the compounds in which ionic radius of R^{3+} $r_R < r_{Dy}$ preserve orthorhombic while those with $r_R > r_{Dy}$ have the tetragonal structure. The Dy-compound can be stabilized in both the orthorhombic and the tetragonal structures with the same oxygen content, depending on the heat treatment. The superconducting properties are found to be very similar for both phases.

In this paper, the review of the low-temperature specific-heat measurements of R123O$_{7-x}$ compounds and the Sr-substituted compounds RBaSrCu$_3$O$_{7-x}$ (R = Sm, Dy, and Er) is presented. The specific-heat data obtained on single-crystalline samples of R123O$_{7-x}$ (R = Sm, Er) in the external magnetic field were analyzed within the CEF approach which allow for the correction of the CEF parameters for Er^{3+} and Sm^{3+} ion in these compounds.

2. Specific heat of RBa$_2$Cu$_3$O$_{7-x}$

For fully oxidized samples R123O$_{7-x}$ (i.e. $x < 0.1$), in spite of different magnitude of magnetic moments, very sharp peaks in the specific-heat curves at low temperature are always observed indicating the transition to the long-range (antiferro)magnetically ordered state, with involved entropy of $R \ln 2$ [7, 10]. The Néel temperature T_N is 0.55 K (for Nd), 0.6 K (for Sm), 0.95 K (for Dy), 0.6 K (for Er). In R123O$_{7-x}$ compounds the magnetic two-ion interactions are expected to be very small, and the CEF interaction plays an essential role in determining the magnetic ground state. The thermal and magnetic properties of these compounds are well described within CEF approach. The CEF contribution to the specific heat is usually calculated by considering a standard Hamiltonian for the orthorhombic symmetry [7, 8, 11, 12]:

$$H_R = \sum_{n=1}^{3} \sum_{m=0}^{n} B_{2n}^{2m} O_{2n}^{2m} + g\mu_B J(-\lambda g\mu_B \langle J \rangle + B_{ext}). \tag{1}$$

The first term is the CEF Hamiltonian written for the lowest multiplet given by Hund's rules. For the orthorhombic symmetry it contains 9 parameters B_{2n}^{2m}. The second term represents the exchange interactions between the magnetic moment $g\mu_B J$ of the R^{3+} ion and the interaction with the external applied magnetic field B_{ext} written in the mean-field (MF) approximation. The corresponding set of energy levels split by the CEF and external field can be obtained by diagonalizing the Hamiltonian (1). In case of a single crystal, we consider the second term in the Hamiltonian (1) in two possibilities of the alignment of the magnetic field: parallel $(g\mu_B J_z B_{ext})$ and perpendicular $(g\mu_B J_x B_{ext})$ to the c-axis of the crystal. For a

comparison with the data obtained on a polycrystalline sample, we have to apply an averaging procedure: the average value ΔC is estimated as $\Delta C = (\Delta C_z + 2\Delta C_x)/3$, where ΔC_z and ΔC_x were calculated respectively for two possibilities of the alignment of the magnetic field [12].

The Er^{3+} ions have a total angular momentum $J = 15/2$ ($S = 3/2, L = 6$ and the Landé factor $g = 6/5$). The CEF interactions split the 16-fold degeneracy of the ground-state multiplet $^4I_{15/2}$ into eight Kramers doublets. INS studies have revealed CEF transitions at 0, 108, 113, 125, 799, 841, 887 and 930 K for $Er123O_7$ [3]. The specific-heat $C(T)$ measurements on single-crystalline sample have revealed the anisotropy ratio of 2.0 of the effective gyromagnetic factors [13]. The sets of CEF parameters reported in Ref. [3] give much lower anisotropy ratio. From the analysis of the $C(T)$ data, a new set of CEF parameters is derived, as listed in Table. We notice here that this set is similar to our previous set [7, 12], but the signs of the B_2^2, B_4^2, B_6^2 and B_6^6 were changed. The two sets of CEF parameters for Er-compound reproduce exactly the same energy splitting, which is in very good agreement with the INS observations [3] (see Table). The Er-moment amounts to $4.38\mu_B$ lying in the ab-plane. These two sets with different sign of B_2^2, B_4^2, B_6^2 and B_6^6, in fact are obtained by taking into account the transformation of spin operators on rotation of the axis [14]. The new set, listed in Table, ensures the easy-direction along the b-axis (i.e. bigger lattice parameter in the ab-plane), whereas the previous set provides a-axis as the easy axis. The MF coefficient $\lambda = -0.05$ T$/\mu_B$ has been chosen to provide the Néel temperature T_N of 0.6 K [7]. This set yields $g_\parallel^{eff} = \Delta/B_\parallel = 2.88$ and $g_\perp^{eff} = \Delta/B_\perp = 5.88$ (Δ denotes the energy separation of the doublet levels) resulting in the effective gyromagnetic ratio $g_\perp/g_\parallel = 2.0$, in very good agreement with the experimental value. The calculated contribution of the Er^{3+} ion to the specific heat of $Er123O_7$ in applied magnetic field along the c-axis reproduces well the experimental results, as shown in Fig. 1. Below 0.6 K, all the doublets are split by exchange interactions which are relevant to an internal field of 0.22 T. The splitting of the ground-state doublet amounts to 1.3 K at 0 K. This splitting produces a magnetic singlet ground state with the ordered magnetic moment of $4.4\mu_B$ aligned along the b-axis, reproducing the Mössbauer value of $(4.2 \pm 0.1)\mu_B$ [15].

For the Sm^{3+} ions with the total angular momentum $J = 5/2$ ($S = 5/2$, $L = 5$ and the Landé factor $g = 2/7$), the 6-fold degeneracy of the ground-state multiplet $^6H_{5/2}$ splits into three Kramers doublets. INS studies of $Sm123O_{7-x}$ compound have revealed two CEF transitions in the ground-state multiplet between the three subsequent CEF levels which are at the same energy transfer of 12 meV (=139 K) [4]. Thus the overall CEF energy splitting amounts to 278 K. The specific-heat measurements performed on single-crystalline sample [16] show a broad anomaly around 1 K, which is typical of the samples with intermediate oxygen range (i.e. $x \approx 0.2$ [6]). Under the applied magnetic field of 8 T along the c-direction ($B \parallel c$) the anomaly is shifted to higher temperature of 1.23 K, whereas almost no influence on the position of the anomaly was observed with applying field perpendicular to the c-direction ($B \perp c$). This anomaly is typical Schottky-type anomaly characteristic of a two-level system with entropy saturat-

TABLE

Sets of CEF parameters for $RBa_2Cu_3O_7$ compounds. E_{1n} are the CEF transitions obtained from INS studies [1–5] and from our CEF calculations (in brackets). Some magnetic characteristic parameters of these compounds resulting from our calculations are given. Notice that the set of CEF parameters for Er-compound (here and in Ref. [7]) give exactly the same CEF levels and similar magnetic characteristics. But the present set gives b-axis as easy direction (see text).

RE	Sm [4, 8]	Dy [2, this paper]	Er [3, 7, this paper]
B_2^0 [K]	+9.85	−1.2	+0.50
B_2^2 [K]	+6.45	−0.51	−0.250
B_4^0 [mK]	−216	+16	−16.95
B_4^2 [mK]	−2160	−1.1	−5.284
B_4^4 [mK]	−2080	−73.6	+87.76
B_6^0 [mK]	0	+22	+85.50
B_6^2 [mK]	0	−13	+80
B_6^4 [mK]	0	+0.67	+2.50
B_6^6 [mK]	0	+9	−25.4
E_{12} [K]	136 (139.6)	43 (43)	108 (107)
E_{13} [K]		59 (58)	113 (114)
E_{23} [K]	139 (139.6)		
E_{14} [K]		153 (154)	125 (126)
E_{15} [K]		188 (187)	799 (795)
E_{16} [K]		– (422)	841 (844)
E_{17} [K]		– (600)	887 (889)
E_{18} [K]		– (621)	930 (931)
λ [T/μ_B]	–	−0.027	−0.05
GS splitting [K]	2.3	1.8	1.3
T_N	–	0.95	0.6
magnetic moment [μ_B/ion]	0.07 (c-axis)	7.1 (c-axis)	4.4 (b-axis)

ing at the expected value of $R\ln 2$. The energy splitting ΔE is estimated to be of 2.3 K in zero applied field and in field of 8 T for $B \perp c$, and ΔE is of 2.8 K in field of 8 T for $B \parallel c$. Because of very small moment of the Sm^{3+} ion, the magnetic neutron diffraction has failed so far to unravel the details of the magnetic structure of Sm-compound. However, our specific-heat results indicate that the c-axis is the easy direction. In the first attempt to analyze the $C(T)$ data of $Sm123O_{7-x}$ compound, the set of CEF parameters derived from INS studies [4] was considered. However, this set produces the splitting of 3.75 K for applying field of 8 T along the c-direction, implying a maximum of the specific-heat anomaly at temperature
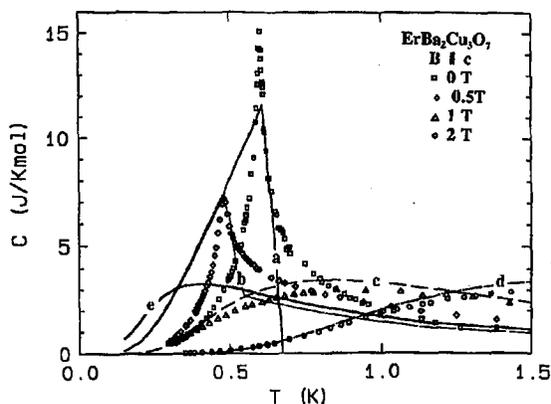
Fig. 1. Specific heat of $ErBa_2Cu_3O_7$ for different magnetic fields applied parallel to the c-direction. Lines represent the calculated curves. See details in Ref. [7].

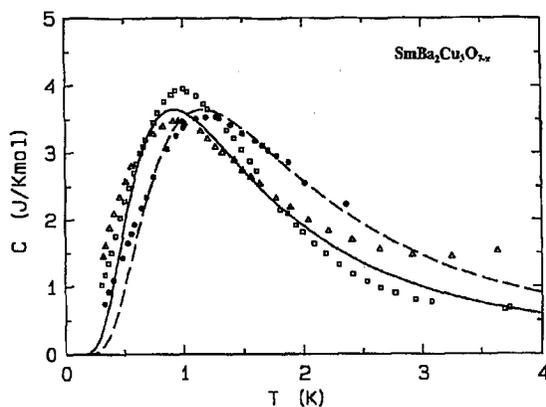Fig. 2. The measured (markers) [16] and calculated (lines) [8] specific heat of $SmBa_2Cu_3O_{7-x}$ ($x \approx 0.2$) for applied magnetic field of 0 T ($\triangle$, solid line), and of 8 T parallel ($\bullet$, broken line) and perpendicular ($\square$, coincide with solid line) to the c-direction.

of 1.6 K, much higher than the observed one. Moreover, this set implies quite big field-effect for field applied perpendicular to the c-direction. From the analysis of our $C(T)$ data, we derived the set of CEF parameters for this compound [8], as listed in Table. This set reproduces the CEF transitions at 139.6 and 279 K, in good agreement with INS observations. The calculated specific heat for both applied field directions is shown in Fig. 2. The ground state has very weak magnetic characteristics with the easy magnetic direction along the c-direction. The internal field at the Sm site accounted for the GS splitting is estimated to be 30 T. The saturation moment amounts to $0.07\mu_B$ [8].

For the analysis of the higher temperature $C(T)$ data, the specific heat is considered to be the sum of a linear term (γT), a cubic (phonon) term βT^3,
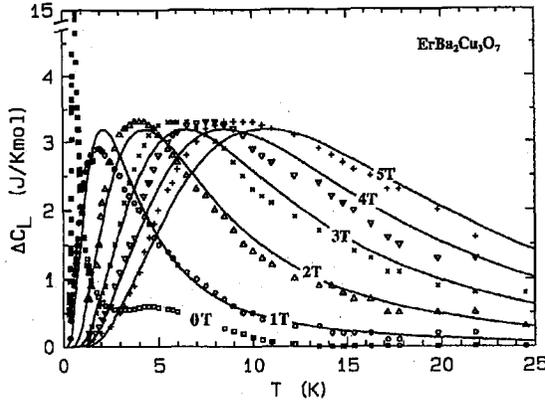
Fig. 3.   Temperature and field dependence of ΔC_L for $ErBa_2Cu_3O_7$ compound in magnetic fields [17]. Solid lines represent the CEF calculations [12].
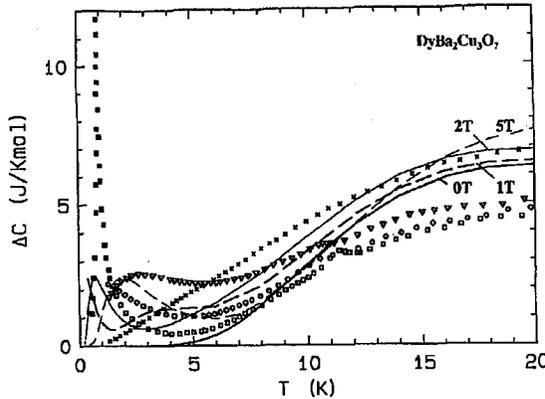

Fig. 4.   Temperature and field dependence of ΔC for $DyBa_2Cu_3O_7$ compound in magnetic fields of 0 T (■ [10], □ [17]), 1 T (○), 2 T (▽) and 5 T (×) [17]. Lines represent the CEF contributions resulting from the set of CEF parameters [2].

and a remaining contribution associated with magnetic ordering and crystal-field effects (ΔC). Although the experiments clearly indicate non-zero values for the coefficient γ ($\gamma = 5.5$ mJ/(K^2 mol) for $R = Y \div Lu$), however, the physical origin of the linear (electronic) term is not fully clear and no specific theory is accepted for explanation of this term. Very little magnetic field dependence of this term were observed up to fields of 5 T. The Debye temperature were estimated $\Theta_D = 350$ K for Sm, 316 K for Gd, Yb, and 314 K for heavy R atoms [17]. After subtraction of the linear and the cubic parts, the behavior of ΔC as a function of the magnetic field was studied in detail. Here we present our analysis for Dy123O$_7$ and Er123O$_7$ compounds. In case of Er123O$_7$ compound, besides the low-temperature anomaly associated with the magnetic ordering, the high-temperature anomaly related with

the CEF contributions from the excited energy levels around 100 K above the lowest doublet level was observed. This additional high-temperature contribution is well separated which can be subtracted in order to discuss the behavior of the low-temperature contributions (ΔC_L) in detail. We show in Fig. 3 the field and temperature dependence of the specific heat ΔC_L of Er-compound, which are of the Schottky-type behavior related to a two-level system (the entropy involved is $R\ln 2$). Good agreement between calculations with the experimental data is obtained, particularly the Schottky anomaly. The slight deviation from a Schottky behavior is ascribed to the magnetic anisotropy. For Dy123O$_7$ compound, the entropy below 20 K exceeds $R\ln 2$, and the complex temperature behavior of ΔC was observed due to the contributions of several energy levels. For this compound, four (GS) CEF transitions at 43 K, 59 K, 153 K and 188 K have been observed and two quite similar sets of CEF parameters have been reported [2]. The set with three determined parameters B_n^0 and the remaining CEF parameters, calculated from the geometry of the nearest-neighboring coordination polyhedra γ_{2n}^{2m} [1], is listed in Table. The MF coefficient λ of -0.027 T/μ_B has been chosen to provide the Néel temperature T_N of 0.95 K [18]. This set provides a very strong anisotropy with the estimated gyromagnetic ratio $g_\parallel/g_\perp$ of 12. The calculated temperature and field dependence of the specific heat ΔC of this compound is shown in Fig. 4. This set reproduces a low-energy splitting in a field of 2 T, however, at much lower temperature. Moreover, this splitting is still present in a field of 5 T, in contrary with the observations [17]. The measurements on single-crystalline Dy-sample is very necessary in order to find the correct set of CEF parameters.

3. Specific heat of $RBaSrCu_3O_{7-x}$ compounds

The oxygen deficiency in these compounds was estimated to be $x \approx 0.07$ [7]. For the light rare earth compounds (R = Nd, Sm), the substitution of Ba by Sr causes the change from the orthohombic to tetragonal structure. The specific heat of these two compounds shows very similar behavior [18]. The sharp peak at T_N of 0.6 K with the entropy of almost $R\ln 2$ disappears by the Sr substitution and only a broad anomaly around 0.6 K is observed, as shown in Fig. 5. Our calculations show that the $C(T)$ data of these two Sr-substituted compounds follow a Schottky-type curve for a two-level system with an energy splitting ΔE of 1.4 K. This splitting is expected to originate from the Kramers doublet ground state, since the excited energy level is located at 100 K above the GS doublet level. We notice here that the Sr substitution as well as the oxygen reduction imply quite similar effect: the disappearance of the long-range order due to the weakening of the exchange interactions between the R^{3+} ions. However, the Sr substitution causes no shift in the position of the specific-heat anomaly, whereas the oxygen reduction implies that the anomaly becomes broader and shifts to higher temperature indicating the bigger splitting of the ground state.

The specific heat of Dy- and ErBrSrCu$_3$O$_7$ compounds are shown in Fig. 6. In contrary with Nd- and Sm-compounds, the Sr substitution only gives very small effect in these two compounds. The long-range magnetic order shown by the sharp peak in the specific heat does still exist. The Sr substitution results in an enhancement of T_N (from 0.95 K to 1.2 K) for the Dy-compound. We notice
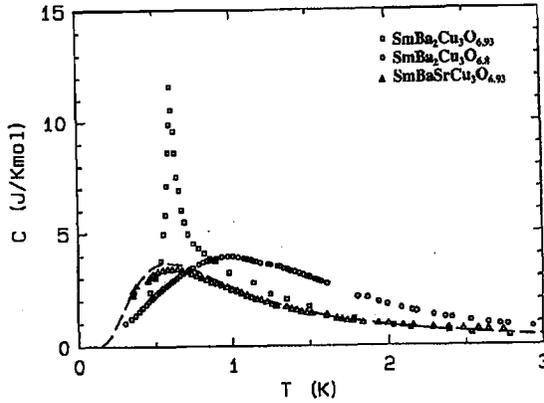
Fig. 5.   Specific heat plotted as C vs. T for $SmBaSrCu_3O_{7-x}$ compound. The data for $Sm123O_{7-x}$ compounds are taken from Refs. [10, 18]. The dotted line represents the Schottky anomaly with an energy splitting ΔE of 1.4 K.
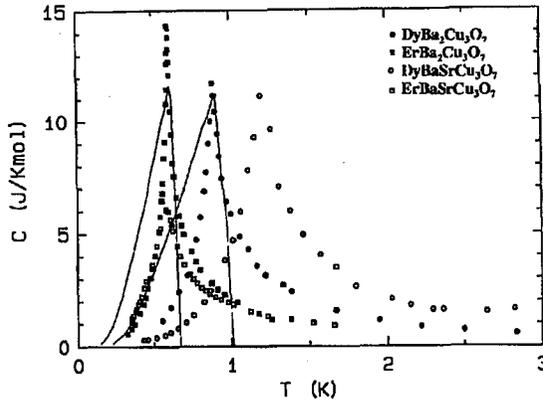

Fig. 6.   Specific heat plotted as C vs. T for $RBaSrCu_3O_7$ (R = Dy, Er). The data for $R123O_7$ compounds are taken from Ref. [7, 10]. Lines represent the CEF calculations with $\lambda = -0.027$ T/μ_B and -0.05 T/μ_B respectively for Dy- and $Er123O_{7-x}$ compounds (see text).

here that the Dy-compound can be stabilized also in the tetragonal structure depending on the heat treatment. However, the $C(T)$ data are almost the same for both Dy-compounds, except for a slight downward shift of T_N of 0.1 K [18]. The entropy reaches the value of $R\ln 2$ in these compounds. The Dy magnetic moments lie along the c-axis, and thus the change of the anisotropy in the ab-plane due to tetragonal-orthorhombic phase transition would not affect the magnetic properties. The enhancement of T_N by the Sr substitution in $DyBaSrCu_3O_7$ compound implies a higher MF coefficient of -0.035 T/μ_B [18]. The $ErBaSrCu_3O_7$ compound remains the orthorhombic structure. The Sr substitution causes only a broadening of the

λ-type of peak at T_N, possibly related to the change of the anisotropy ratio in the *ab*-plane. The entropy reaches only 70% of $R\ln 2$ in this case. As the Néel temperature is the same at 0.6 K, we expect that for $ErBaSrCu_3O_{7-x}$ the magnetic singlet ground state is produced by the (same) weak exchange interactions of -0.05 T$/\mu_B$, as in Er123O$_7$ compound.

4. Conclusion

Our analysis shows that the specific-heat measurements on single-crystalline samples in applied magnetic field are particularly useful for the correct evaluation of the CEF parameters in the high-T_c superconductors $RBa_2Cu_3O_{7-x}$. The new set of CEF parameters for Sm and the corrected one for Er-compounds, give very good agreement with the energy level scheme obtained from INS studies. Moreover, they account for all known magnetic properties of these compounds (magnetic moment, susceptibility, anisotropy of the ground state). The specific-heat anomaly at low temperature is a clear indication of the energy splitting of Kramers doublet GS. The mechanism for this splitting, however, is still puzzling. In case of Dy123O$_7$ and Er123O$_7$ compounds, the energy splitting is caused by an internal magnetic field of less than 1 T, whereas the field of 30 T is necessary to account for the energy splitting in Sm123O$_7$ compound. The substitution of Ba by Sr causes a significant influence on the structural and magnetic properties of the $RBaSrCu_2O_7$ compounds for the light rare earth (R = Nd, Sm), whereas only a small effect is observed for the heavy one (Dy, Er).

Acknowledgments

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