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Magnetic specific heat and susceptibility measurements on $NdBa_2Cu_{3-x}Ga_xO_{7-y}$ at low temperatures☆

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Abstract

We report on the temperature dependence of magnetic specific heat and magnetic susceptibility results on Ga-substituted Nd-123 compounds at low temperatures. The magnetic ordering of the Nd^{3+} ions changes remarkably with increasing Ga concentration. The results are similar to those reported for pure undoped $NdBa_2Cu_3O_{7-y}$ samples when the oxygen content is reduced. The nature of the magnetic ordering is analysed using different magnetic models and the importance of crystalline electric field effects, in determining the nature of magnetic ordering, is emphasised.

Keywords: Magnetism; Neodymium; Specific heat

1. Introduction

The co-existence of magnetism and superconductivity in high-temperature superconductors has been extensively investigated by various researchers [1, 2]. In particular the effect of varying the oxygen concentration on the magnetic ordering of the rare earth ion (RE) was studied by specific heat and neutron scattering measurements [3]. There is a systematic and marked variation of the shape and temperature of ordering of RE ions like Nd, Sm, etc., with the variation of oxygen content, essentially due to change of the in-plane (Cu–O) carrier concentration. The influence of oxygen

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stoichiometry on the magnetic ordering of Nd^{3+} is strongest in $NdBa_2Cu_3O_{7-y}$. However, there are no detailed experiments reporting on the effects of substituting the Cu atoms in the chain-sites and the resulting effects on the magnetic ordering of the Nd^{3+} ions.

Gallium is non-magnetic and substitutes Cu predominantly in the chain site. The effects of Ga substitution on the superconducting properties of RE-123 superconductors have been investigated in detail (with electrical conductivity, susceptibility and partially thermopower experiments) by Mary et al. [4] and Xu et al. [5]. The orthorhombic-to-tetragonal transition (O–T) occurs for a Ga concentration of $x > 0.09$; the compounds are non-superconducting above a Ga concentration of $x = 0.25$. The oxygen content of the samples prepared were in the range $0.05 < y < 0.1$. The decrease of the superconducting transition temperature T_c, due to doping Nd-123 samples with Ga, is more drastic in comparison to the effect of Ga doping in other RE-123 superconductors. The reduction of T_c in these compounds may be attributed to the hole-filling mechanism. For these reasons, we have chosen Ga to substitute Cu on the chain-site in Nd-123. Thus, the influence of different Ga contents on the change in magnetic ordering of Nd^{3+} ions and on the decrease of the superconducting transition temperature was studied simultaneously by d.c. electrical conductivity, heat capacity, magnetic susceptibility and neutron scattering experiments, and also crystalline electric field analysis [6, 7].

In this contribution, we report on the magnetic specific heat of some Ga-substituted Nd-123 compounds, $NdBa_2Cu_{3-x}Ga_xO_{7-y}$, in the temperature range from 1 to 5 K. Part of this work is contained in a much more comprehensive report, which details the sample preparation and the determination of the magnetic heat capacity from the measured value [6].

2. Experimental

The samples were prepared as described in Refs. [4] and [6]; the characterization of the single-phase samples was carried out as reported in Ref. [6]. Heat capacity measurements were performed using a quasi-adiabatic Nernst-type step-heating method in the temperature range from 0.45 to 100 K [8]. Different calorimeters were applied for the ranges of liquid ^3He and ^4He. A multiple sample holder arrangement for heat capacity measurement, enabling measurement of three samples during one cooling procedure, has been designed and developed for this purpose. The d.c. magnetic susceptibility measurements have been carried out employing a Quantum Design SQUID magnetometer in the temperature range between 2 and 350 K, and applying magnetic fields of 1–2 Tesla in the normal state and 5–10 mTesla in the superconducting state.

3. Results and data analysis

The specific heats of the compounds were computed from the measured total heat capacity C of the samples after correcting for the sample holder heat capacity. The

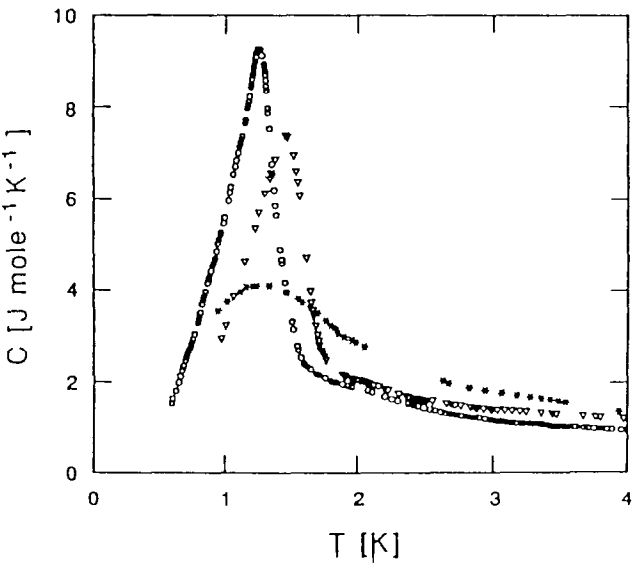

Fig. 1. Magnetic specific heats of: ★, $NdBa_2Cu_{2.7}Ga_{0.3}O_{7-y}$; ○, $NdBa_2Cu_{2.5}Ga_{0.5}O_{7-y}$; and ▽, $NdBa_2Cu_{2.5}Ga_{0.5}O_{6.2}$.

magnetic specific heats were derived from the sample's specific heat C_p by subtraction of the T^3 lattice and linear terms. The lattice as well as the linear contributions were determined by plotting C/T vs. T^2. The magnetic specific heats C_m, thus obtained and plotted in Fig. 1, show pronounced anomalies below 2 K. The highly Ga-doped compound with $x = 0.5$ displays a sharp peak at 1.33 K, whereas the less doped sample with $x = 0.3$ shows a broad, bell-shaped anomaly centered at 1.24 K. The undoped, but oxygen-deficient compound $NdBa_2Cu_3O_{6.2}$, ($x = 0$, $y = 0.8$) orders at 1.51 K, in agreement with the reported values [3]. We note that the undoped, fully stoichiometric compound $NdBa_2Cu_3O_{7-y}$($y \sim 0$) orders at $T_N = 0.53$ K.

The Nd^{3+} ion is a Kramers ion with a ground-state doublet. All the excited levels occur far away from the ground state, above 100 K. Hence the observed specific heat anomalies are of magnetic nature and are attributed to spin-1/2 system. We have analysed the anomalies with different magnetic models using different lattice dimensionalities.

The sharp magnetic anomaly of the compound $NdBa_2Cu_{2.5}Ga_{0.5}O_{6.94}$ clearly indicates long-range magnetic order of three-dimensional (3D) character. A more refined way to determine the nature of the magnetic ordering is an analysis of the critical exponent [9]. For such an analysis, a plot of $\ln|1 - T/T_N|$ vs. $\ln|C_m/R|$ is shown in Fig. 2. In this graph, the slope of the straight line portion above $T > T_N$ is least-square fitted. The fit yields a critical exponent of -0.83. This value is closer to the value of -1 expected for an isotopic spherical model than for a three-dimensional Ising model, for which the critical exponent lies between $-1/8$ and $-/16$. The coupling constant of the magnetic interaction was calculated using the T^3 dependence of the magnetic spin wave contribution to the specific heat below T_N. The isotropic coupling constant amounts to 0.54 K.

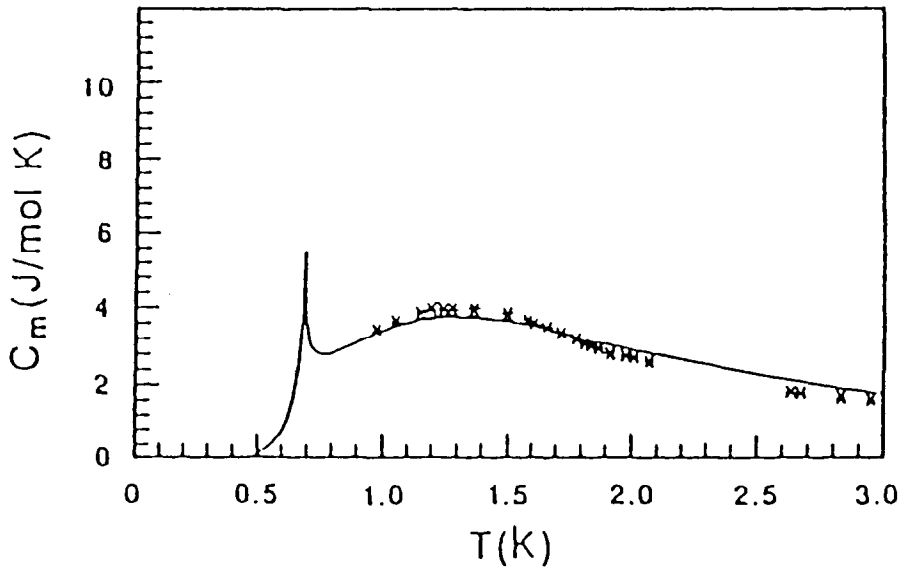

Fig. 2. $NdBa_2Cu_{2.5}Ga_{0.5}O_{7-y}$. Plot of $\ln(C_m/R)$ vs. $\ln(1 - T/T_N)$ for the determination of the critical exponent of magnetic ordering.

The rather broad anomaly found for $NdBa_2Cu_{2.7}Ga_{0.3}O_{7-y}$ is best represented by a two-dimensional (2D) anisotropic Ising model [10]. The data, together with the theoretically fitted curve, are given in Fig. 3. The coupling constants, resulting from the fit are $E_1 = 1.55$ K and $E_2 = 0.0074$ K.

The undoped oxygen-rich compound $NdBa_2Cu_3O_{7-y}$ (with $y = 0.06$) orders antiferromagnetically with a sharp transition at 0.53 K [3]. The nature of the anomaly is best represented by a two-dimensional anisotropic Ising model with an anisotropy parameter greater than 50. In contrast to that, the largely oxygen-deficient sample, $NdBa_2Cu_3O_{6.2}$, orders at a much higher temperature at $T_N = 1.51$ K. Inspection of the specific heat curve indicates that the magnetic ordering has a three-dimensional Ising character.

The temperature dependence of the inverse susceptibilities of $NdBa_2Cu_{3-x}Ga_xO_{7-y}$ samples with $0 < x < 0.5$ and $0.05 < y < 0.1$ shows clear deviations from a Curie–Weiss behaviour at low tempeatures which are attributed to crystalline electric field (CEF) effects [11]. The inverse susceptibilities as a function of temperature were analysed in terms of CEF effects from different site symmetry. A systematic analysis using the CEF hamiltonians of Penny and Schlapp [12] and Lea et al. [13] lead to a dramatic and unusual reduction in the diagonal parameters, $B(4,0)$ and $B(6,0)$, near the O–T transition. This fact is taken as evidence for a strong change in the crystalline electric field anisotropy. The fall in the B parameters is also verified by independent point-charge calculation from the structure data [14]. The reduction of the diagonal

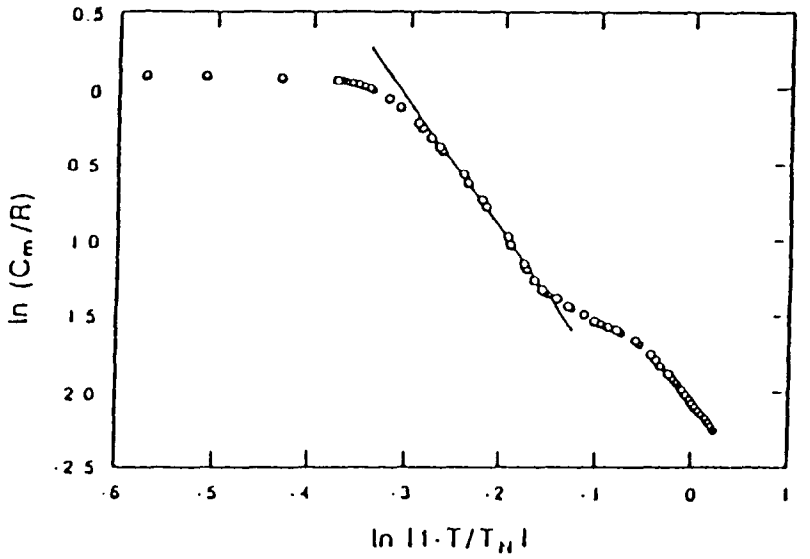

Fig. 3. $NdBa_2Cu_{2.7}Ga_{0.3}O_{7-y}$. Experimental (○) and theoretical (—) magnetic specific heats, the latter calculated for a 2D-Ising model.

parameters suggests that the magnetic anisotropy parameter decreases with increasing Ga concentration.

4. Discussion and conclusions

The magnetic ordering of $NdBa_2Cu_{3-x}Ga_xO_{7-y}$ with $x = 0.3$ and 0.5 lies between that of the oxygen-deficient and oxygen-rich compounds. The overall changes in the magnetic ordering temperature and the temperature dependence of the magnetic specific heat, introduced by the Ga substitution, strongly resembles those observed for Nd-123 compounds with different oxygen contents [3, 15]. Increasing the Ga content x on the Cu chain site (for $y = 0$) induces changes in the magnetic properties, including the effect on the dimensionality of magnetic ordering, in the same way as observed when the oxygen content y is decreased in undoped ($x = 0$) Nd-123 samples. The nature of the magnetic ordering changes from a 2D-Ising to a 3D mean-field-like behaviour when x is increased from 0 to 0.5 with $y = 0.06$, whereas it is a 3D-Ising type for the oxygen-deficient, undoped compound [6]. The fact that the magentic ordering changes from an anisotropic nature (2D, even 1D-like for compounds with $y \geq 0.1$, or 3D-Ising) for the superconducting samples, to 3D isotropic ordering for non-superconducting samples, is supported by the CEF analysis of magnetic susceptibility data [16]. The analysis clearly indicates a reduction of the diagonal parameters, reminiscent of a reduction of the magnetic anisotropy parameter. These results indicate the importance of CEF effects in determining the nature of the magnetic ordering of Nd^{3+} ions in these compounds.

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References

[1] A.V. Narlikar, Substitutional studies on high temperature superconductors, in A.V. Narlikar (Ed.), Studies of High Temperature Superconductors, Nova Science Publishers, New York, 1989 and 1992.
[2] J.T. Margret, Rare earth and other substitutions in high temperature oxide superconductors, in D.M. Ginsberg (Ed.), Physical Properties of High Temperature Superconductors, World Scientific, Singapore, 1989.
[3] P. Allenspach, J. Appl. Phys., 73 (1993) 6317.
[4] T.A. Mary and U.V. Varadaraju, Bull. Mater. Res., 27 (1992) 447.
[5] W. Xu and W. Guan, Physica C, 212 (1993) 119.
[6] A.M. Niraimathi, E. Gmelin and G. Rangarajan, Phys. Rev. B, 51 (1995) 8503.
[7] A.M. Niraimathi, Indian J. Appl. Phys., 29 (1991) 307.
[8] E. Gmelin and P. Roedhammer, J. Phys. E.: Sci. Instrum., 14 (1981) 223.
E. Gmelin and K. Ripka, Cryogenics, 21 (1981) 117.
[9] D.G. Onn, H. Meyer and J.P. Remeika, Phys. Rev., 156 (1967) 663.
[10] D.C. Matthis, Theory of Magnetism, Springer-Verlag, Berlin, 1986.
[11] Prior to any analysis, the susceptibility of Y-123 is subtracted from the measured susceptibilities in order to detect the copper magnetic moments. The diamagnetic core corrections are also taken into account so that the deviations in the inverse susceptibilities are fully attributed to the CEF effects on the Nd^{3+} ions.
[12] W.G. Penny and R. Schlapp, Phys. Rev., 41 (1932) 194.
[13] K.R. Lea, M.J.M. Leask and W.P. Wolf, J. Phys. Chem. Solids, 23 (1962) 1381.
[14] M.T. Hutchings, in F. Seitz and H. Turnball (Eds.), Solid State Physics, Vol. 16, Academic Press, New York, 1964.
[15] P. Allenspach, B.W. Lee, D. Gajewski, M.B. Maple, S.I. Yoo and M.J. Kramer, J. Appl. Phys., 73 (1993) 6317.
[16] A.M. Niraimathi, Ph.D. Thesis, Indian Institute of Technology, Madras.