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Influence of Ga Substitution on the Magnetic Ordering of Nd Ions in $NdBa_2Cu_{3-x}Ga_xO_{7-y}$ at Low Temperatures

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Abstract: The temperature dependence of magnetic specific heat and magnetic susceptibility of Ga substituted Nd-123 compounds has been investigated at low temperatures. The magnetic ordering of the Nd^{3+} ions changes remarkably with the Ga concentration. The nature of the magnetic ordering is analysed using different magnetic models. The results are compared with those reported for pure unsubstituted $NdBa_2Cu_3O_{7-y}$ samples with various oxygen contents. The magnetic susceptibility data are analysed in the light of crystalline electric field effect (CEF) of different symmetry. The importance of CEF effects in determining the nature of magnetic ordering is explained.

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 oxygen variation on rare earth ion (RE) magnetic ordering was studied by magnetic specific heat and neutron scattering measurements.[3] There is a systematic and marked variation of the shape and ordering temperature of RE-ions like Nd, Sm, etc. with the variation of oxygen content. The influence of oxygen stoichiometry on the magnetic properties is strongest in $NdBa_2Cu_3O_{7-y}$. However, there exist no detailed experiments reporting on the effects of substitution of Cu in the Cu-chains and the resulting effects on the magnetic ordering of the Nd^{3+} ions.

Gallium is non-magnetic and *substitutes predominantly Cu 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 decrease of the superconducting transition temperature T_c, due to substitution of Nd-123 samples with Ga, is more drastic in comparison to the substitutional effect in other RE-123 superconductors. The reduction of T_c in these compounds may be attributed to the hole filling mechanism. For the above given reasons, we have chosen Ga, to substitute Cu in Nd-123, for a detailed investigation of the effect of different Ga contents on the magnetic ordering of Nd^{3+} ions. Simultaneously, the change of the magnetic ordering of Nd^{3+} ions with the decrease of the superconducting transition temperature was studied. In this contribution, we report on *magnetic specific heat* and *magnetic susceptibility* measurements of Ga substituted Nd-123 compounds, $NdBa_2Cu_{3-x}Ga_xO_{7-y}$, in the temperature range from 1 to 5 K.

2 SAMPLE PREPARATION AND CHARACTERIZATION

The samples were prepared by the usual solid state reaction method and characterized for single phase, oxygen stoichiometry and composition; the details of sample characterization are reported elsewhere.[6] The orthogonal-to-tetragonal transition (O–T) occurs for a Ga-concentration of $x > 0{\cdot}09$; the compounds are non-superconducting

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above a Ga concentration of $x = 0{\cdot}25$. The oxygen content of the samples prepared were in the range $0{\cdot}05 < y < 0{\cdot}1$. For the samples used, other physical properties were also measured, temperature dependence of dc resistivity and dc magnetic susceptibility.[7]

3 EXPERIMENTAL

Heat capacity measurements were performed using a quasi-adiabatic Nernst-type step heating method in the temperature range from 0·45 K to 100 K.[8] Therefore different calorimeters were applied for the ranges of liquid ^{3}He and ^{4}He. A multiple sample holder arrangement for heat capacity measurement, enabling measurement of three samples during one cooling procedure, has been designed and developed for that purpose. The dc magnetic susceptibility measurements have been carried out employing a Quantum Design SQUID magnetometer in the temperature interval between 2 and 350 K, and applying magnetic fields of 1–2 T in the normal state and 50–100 Gauss (1 Gauss ≡ 10^{-4} T) in the superconducting state.

4 RESULTS AND DATA ANALYSIS

The specific heats of the compounds were computed from the measured total heat capacity C of the samples after correction for the sample holder heat capacity. The magnetic specific heats were derived from the specific heat C_p of the sample by subtraction of the lattice and, at low temperatures ($T < 5$ K), 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 $x = 0{\cdot}5$ displays a sharp peak at 1·33 K, whereas the low substituted sample with $x = 0{\cdot}3$ shows a broad, bell shaped anomaly centred at 1·24 K. The unsubstituted, but oxygen-deficient compound, $NdBa_2Cu_3O_{6\cdot2}$ $x = 0$, $y = 0{\cdot}8$ orders at 1·51 K, in agreement with the reported values.[3] We note that the unsubstituted, fully stoichiometric compound, $NdBa_2Cu_3O_{7-y}$ ($y \sim 0$) orders at $T_N = 0{\cdot}53$ K.

The Nd^{3+} ion is a Kramer 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 a spin 1/2 system. We have analysed the anomalies with different magnetic models using varying spin dimensionalities.

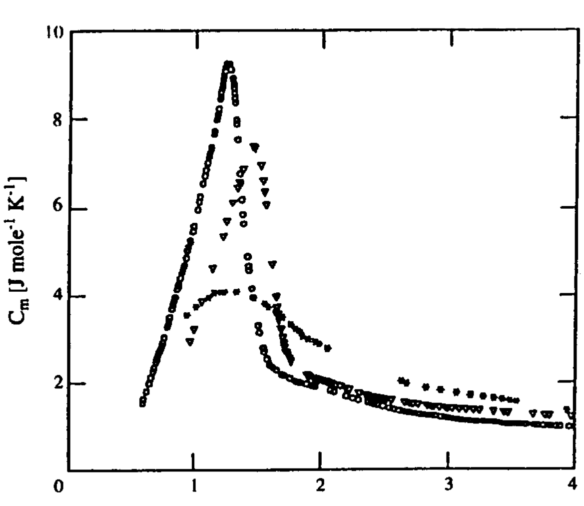

Fig. 1. Magnetic specific heat of: (★★★★) $NdBa_2Cu_{2\cdot7}Ga_{0\cdot3}O_{7-y}$; (OOOO) $NdBa_2Cu_{2\cdot5}Ga_{0\cdot5}O_{7-y}$; (∇∇∇∇) $NdBa_2Cu_{2\cdot5}Ga_{0\cdot5}O_{6\cdot2}$.

4.1 Compound $NdBa_2Cu_{2\cdot5}Ga_{0\cdot5}O_{6\cdot94}$

The sharp magnetic anomaly of this compound clearly indicates *long range magnetic order of three-dimensional character*. A more refined way, to find out the nature of 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 that graph, the slope of the straight line portion above $T > T_N$ is least square fitted. The fit yields a critical exponent of $m = -0{\cdot}83$. This value is closer to the value of -1, expected for an isotropic spherical model than for a three-dimensional Ising model, for which the critical exponent lies between $-1/8$ to $-1/16$. 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 0·5 K.

4.2 Compound $NdBa_2Cu_{2\cdot7}Ga_{0\cdot3}O_{7-y}$

The broad anomaly is best represented by a *two-dimensional anisotropic Ising model*.[10] The data, together with the theoretically fitted curve, are

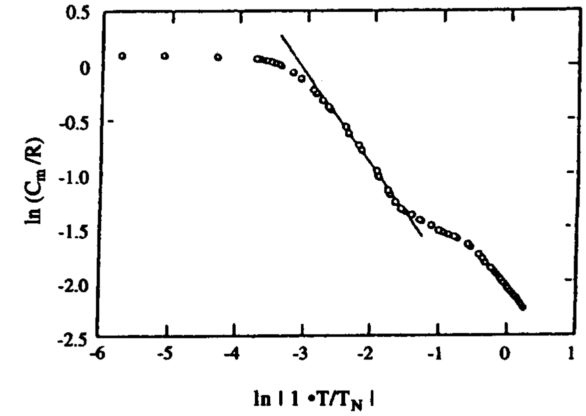

Fig. 2. $NdBa_2Cu_{2\cdot5}Ga_{0\cdot5}O_{7-y}$: Plot $\ln(C_m/R)$ vs $\ln(1-T/T_N)$ for the determination of the critical exponent of magnetic ordering.

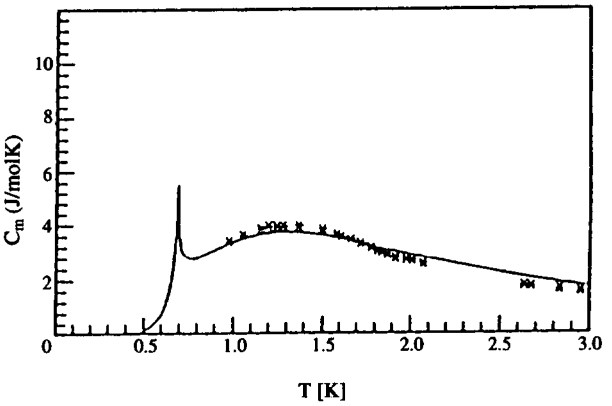

Fig. 3. $NdBa_2Cu_{2.3}Ga_{0.5}O_{7-y}$: Experimental (★★★) and theoretical magnetic specific heat (———), calculated for a 2D-Ising model.

given in Fig. 3. The coupling constants, resulting from the fit, are E_1 = 1·55 K and E_2 = 0·0074 K.

4.3 Compounds $NdBa_2Cu_3O_{7-y}$ and $NdBa_2Cu_3O_{6.2}$ (unsubstituted)

The unsubstituted oxygen-rich compound $NdBa_2Cu_3O_{7-y}$ (with y = 0·06) orders, as reported in literature, antiferromagnetically with a sharp transition at 0·53 K. The nature of the anomaly is best represented by *two-dimensional (2D) anisotropic Ising model* with an *anisotropy-parameter greater than 50.* In contrast to that, the measured largely oxygen-deficient sample, $NdBa_2Cu_3O_{6.2}$, is ordering at much higher temperature at T_N = 1·51 K. Inspection of this specific heat curve indicates that the magnetic ordering has *three-dimensional Ising character.*

4.4 Magnetic susceptibility

The temperature dependence of the inverse susceptibilities of $NdBa_2Cu_{3-x}Ga_xO_{7-y}$ samples with $0<x<0.5$ show clear deviations from a Curie Weiss behaviour at low temperatures that are attributed to crystalline electric field (CEF) effects. Prior to any analysis, the susceptibility of Y-123 is subtracted from the measured susceptibilities 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. The inverse susceptibilities as a function of temperature were analysed in terms of CEF effects from different site symmetries. A systematic analysis using Penny and Schlapp[11] and Lea, Leask and Wolf[12] methods leads to a dramatic change of the diagonal parameters, A(4,0) and A(6,0), near the O–T transition as is shown in Fig. 4(a/b). The drop of the A-parameters is also verified by independent point charge calculation from the structure data.[13] The reduction of diagonal parameter A(4,0) suggests that the *magnetic anisotropy-parameter decreases with the increasing Ga concentration.*

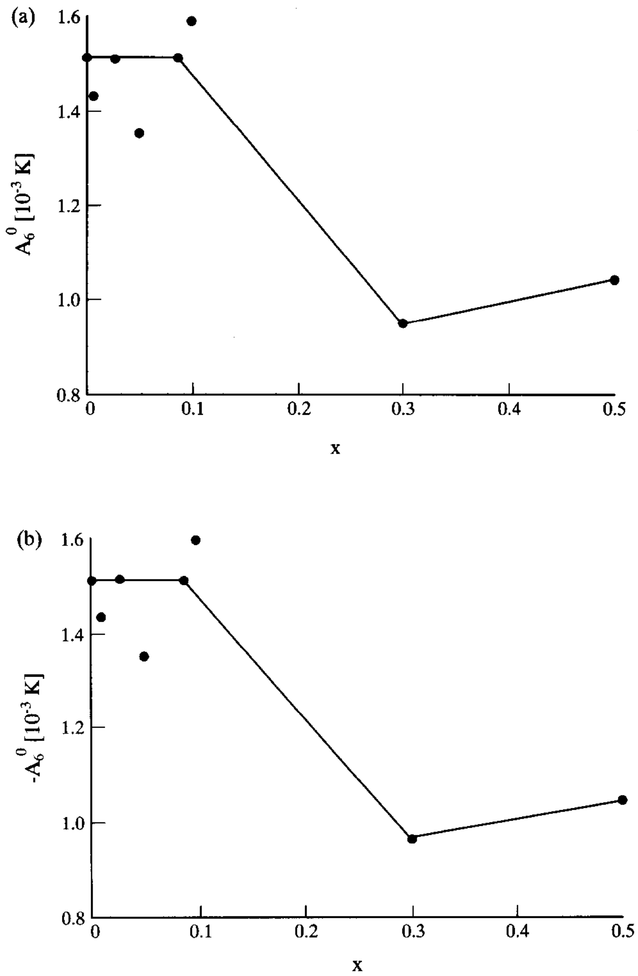

Fig. 4.(a,b) Variation of the crystalline electric field parameters A(4,0) and A(6,0) as a function of Ga-concentration x for $NdBa_2Cu_{3-x}Ga_xO_{7-y}$.

5 DISCUSSION AND CONCLUSIONS

The magnetic ordering of the $NdBa_2Cu_{3-x}Ga_xO_{7-y}$ with x = 0·3 and 0·5 lies between that of the oxygen-deficient and oxygen-rich compounds. The overall changes of the magnetic ordering temperature and temperature dependence of the magnetic specific heat, introduced by the Ga substitution, strongly resemble those observed for Nd-123 compounds with different oxygen contents. The nature of the magnetic ordering changes from 2D-Ising to 3D isotropic behaviour when x is increased from x = 0 to x = 0·5 with y = 0·06, whereas it is of 3D-Ising type for the oxygen-deficient and unsubstituted compound. The fact that the magnetic ordering changes from anisotropic nature (2D-even 1D-like for compounds with $Y \geq 0.1$ — or

3D-Ising), for the superconducting samples, to 3D isotropic, for non-superconducting samples, is supported by the CEF analysis of magnetic susceptibility data. The analysis clearly indicates a reduction of the diagonal parameters, reminiscent of a reduction of the magnetic anisotropic parameter. These results show the importance of CEF effects in determining the nature of the magnetic ordering of Nd^{3+} ions in these compounds.

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