Magnetic ordering of Nd^{3+} ions in the high-temperature superconductor $NbBa_2Cu_{3-x}Ga_xO_{7-y}$ ($0<x\leq 0.5$ and $0.05<y<0.15$)

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We report on the magentic specific heats of $NdBa_2Cu_{3-x}Ga_xO_{7-y}$ measured in the temperature range from 0.45 to 100 K. The Ga substitution in the Cu chain sites descreases the superconducting transition temperature drastically. Simultaneously, there is a systematic increase of temperature of magnetic ordering of the Nd^{3+} ions with Ga substitution. The nature of the magnetic ordering of Nd^{3+} ion changes from two-dimensional (2D) anisotropic Ising behavior for the oxygen rich compound with zero Ga content to 1D Ising-like for low Ga concentration. With higher Ga concentration, at the advent of nonsuperconductivity, long-range (3D) magnetic ordering is reestablished. The increase of the magnetic interaction between the Nd^{3+} ions by the substitution of Ga is discussed with the variation of carrier concentration, increase in the Nd-O bond length and with the additional interaction due to Cu-ion ordering in the nonsuperconducting compounds.

I. INTRODUCTION

Many efforts have been made to understand the coexistence of superconductivity and magnetism in rare-earth 123 (R123) oxide superconductors. It is well known that the R^{3+} ion in R123 superconductors has small effect on the superconducting properties except in the case of Pr.[1,2] Recently, it was found that there is a systematic change of magnetic ordering of R ions like Nd, Sm, Er, and Dy with the amount of the oxygen content in these compounds.[3–5] This variation is found to be maximum in Nd123 superconductor. As the oxygen depletion is in the Cu-chain sites, the oxygen deficiency cannot influence directly the Nd^{3+} ion ordering and the variation of the magnetic ordering is thought to be due to the change in the charge carrier concentration and/or due to the localization of mobile holes.[6]

To understand the effect of the change in the carrier concentration on the magnetic ordering of the Nd^{3+} ion, we selected the Ga-substituted Nd123 system. This compound is chosen because Ga is nonmagnetic, so the T_c depression cannot be accounted for by the pair-breaking mechanism. Moreover, it was reported recently[7,8] that Ga is much more effective in reducing T_c in the Nd123 system compared to the Y123 or Er123 compounds. Hence by studying the Ga-substituted Nd123 system we can study the variation of the magnetic ordering with respect to the change in the charge carrier concentration as well as the change in T_c due to the replacement of Cu by Ga.

In this contribution we report on a systematic investigation of the magnetic ordering of Nd^{3+} ions in Ga-substituted Nd123 compounds, $NdBa_2Cu_{3-x}Ga_xO_{7-y}$ ($0<x\leq 0.5$) by low-temperature heat-capacity measurements in the temperature range from 100 K down to 0.45 K. We observe sharp, and in some cases broad, peaks in $C_P(T)$ at low temperatures. The temperature dependence of the magnetic contribution to $C_P(T)$, its magnetic energy E_m, and the magnetic entropy S_m are analyzed in terms of different models of magnetic ordering. The paper is organized as follows: after a description of sample preparation, characterization, and experimental techniques, we compute the magnetic specific heat, determine coupling constants, discuss the influence of Ga concentration and oxygen deficiency on the magnetic ordering of Nd^{3+} ions and give a phenomenological explanation of the anisotropy of the coupling constants, the variation of the magnetic ordering temperature and the dimensionality with Ga concentration.

II. EXPERIMENTAL DETAILS

A. Sample preparation and characterization

Initially the samples used for the heat-capacity measurements were provided by Mary *et al.*[7] who have already described elsewhere their method of sample preparation. Later large quantities of samples (about 25 g) of $NdBa_2Cu_{3-x}Ga_xO_{7-y}$ were prepared for neutron-scattering measurements. These samples were also used for specific-heat measurements especially below 2 K. The starting materials were high-purity Nd_2O_3 (99.99% pure and preheated at 950 °C for 24 h), BaO_2 (99.99% purity), CuO and Ga_2O_3 (99.999%) which were mixed in stoichiometric proportions in an agate mortar and pestle. The use of 2–3 ml of acetone ensures homogeneous mixing of the materials. The samples were then sintered in an alumina crucible at 920 °C for 24 h and reground. This procedure was repeated 5 to 6 times. The long calculation time ensures high quality of the samples. Final-

ly, the fully calcined samples were pressed at a pressure of 0.5–1 ton/cm^2 using a titanium-coated die with a diameter of 1 cm and the pellets were sintered for 24 h at 920 °C. The low pelletizing pressure facilitates the diffusion of oxygen through the sample. Oxygen (99.999%) treatment was carried out for a long period of 24 h at 900 °C and 5 days at 600 °C with slow rates of heating and cooling (20 °C/h). The characterization and quality testing of the samples were carried out with powder x-ray diffraction (XRD), iodometric titration, and atomic emission spectroscopy (AES) coupled with oxygen gas analysis. The powder x-ray diffractograms obtained using Cu K_α radiation are shown in Fig. 1. The XRD patterns indicate that all the samples were single phase within 5%. The gradual replacement of Cu by Ga causes an orthorhombic to tetragonal (O-T) transition near $x \approx 0.09$. This results in peaks [e.g., the doublet at $(hkl)=(060)$, (200), and (002)] corresponding to orthorhombic symmetry becoming unresolvable until the lattice parameters a and b become identical. The diffractograms were indexed and unit-cell parameters determined by least-squares fitting to standard formulas appropriate to orthorhombic and tetragonal symmetries. The unit-cell parameters are given in Table I. The oxygen content y was estimated by iodometric titration. The values are accurate to within ± 0.05. The compositions were determined by AES, from the masses of the different constituents emitted on heating to about 3000 °C. The AES data are given in Table II.

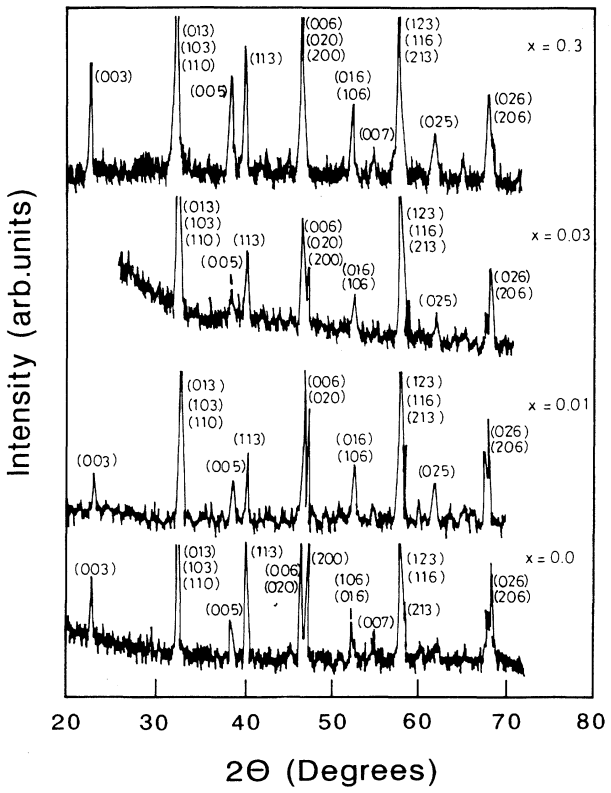

FIG. 1. X-ray powder diffractogram of $NdBa_2Cu_{3-x}Ga_xO_{7-y}$ for different Ga concentrations $x=0$, 0.01, 0.03, and 0.3 with $0.05 < y < 0.15$.

TABLE I. Unit-cell parameters a, b, and c, T_c (onset), T_c (mid), and Meissner fraction for $NdBa_2Cu_{3-x}Ga_xO_{7-y}$ compounds, where x denotes the Ga content.

x (Ga)	a (Å)	b (Å)	c (Å)	T_c (onset) (K)	T_c (mid) (K)	Meissner fraction (%)
0	3.86	3.91	11.78	90.0	89.7	22
0.01	3.86	3.91	11.78	81.5	81.2	25
0.02	3.87	3.91	11.78	82.0	80.2	27
0.03	3.88	3.92	11.77	72.5	70.5	23
0.04	3.88	3.92	11.77	70.0	60.6	18
0.05	3.88	3.91	11.76	63.5	60.0	27
0.06	3.89	3.91	11.76	63.5	56.2	58
0.07	3.89	3.90	11.76	63.5	52.0	60
0.08	3.89	3.90	11.76	64.5	52.4	53
0.09	3.89	3.89	11.76	68.5	50.1	35
0.10	3.90	3.90	11.76	50.5	42.6	54
0.30	3.88	3.88	11.76			
0.50	3.91	3.91	11.76			
$0,y=0.8$	3.90	3.90	11.85			

Additionally, the unsubstituted $NdBa_2Cu_3O_{6.2}$ was prepared by reducing the sintered sample in flowing nitrogen for 65 h at 650 °C. For this compound the oxygen content of $y \approx 0.8$ was estimated by AES. The sample was further characterized by XRD and by checking for the absence of superconductivity by dc susceptibility measurements down to 2 K. The diffractogram indicated a clear tetragonal symmetry (see Table I). The compound $NdBa_2Cu_3O_{6.2}$ was used as a reference material for the investigation of magnetic ordering effects below 2 K. In the case of the superconducting compositions, T_c and the Meissner fraction were determined from the temperature dependence of electrical resistivity $\rho(T)$ and dc magnetic susceptibility $\chi(T)$. Semiautomatic measurements of $\rho(T)$ were performed by the van der Pauw method as described already.[9] The susceptibility $\rho(T)$ was measured using a SQUID magnetometer (Quantum Design). As examples, $\rho(T)$ and $\chi(T)$ curves of some samples are plotted in Figs. 2(a) and 2(b). The inset in Fig. 2(a) shows $d\rho/dT$ vs T for the compound with $x=0.09$. Figure 2(b) displays the field-cooled (FC) and zero-field-cooled (ZFC) susceptibilities in a field of 100 G for the compound with $x=0$. The temperature variation of susceptibility data for all samples and a more detailed discussion on the normal-state susceptibility, with reference to crystalline electric-field effects, in these compounds will be published

TABLE II. Atomic emission spectroscopy (AES) analysis results for the compound $NdBa_2Cu_{3-x}Ga_xO_{7-y}$ with different Ga concentration x.

x (Ga)	Composition
0.01	$NdBa_{1.95}Cu_{2.91}Ga_{0.02}O_{6.9}$
0.03	$NdBa_{1.98}Cu_{2.92}Ga_{0.04}O_{6.85}$
0.3	$NdBa_{1.79}Cu_{2.71}Ga_{0.22}O_{6.87}$
0.5	$NdBa_{1.91}Cu_{2.5}Ga_{0.53}O_{6.94}$
$0,y=0.8$	$NdBa_{1.97}Cu_{2.92}O_{6.17}$

separately.[10] T_c (onset) was determined as the temperature at which a reversal of sign occurs in the slope of $\chi(T)$. T_c (mid) was defined as the temperature at which a peak in $d\rho/dT$ occurs. T_c (onset), T_c (mid), and the Meissner fractions are listed in Table I for the different Ga concentrations.

B. Heat-capacity experiments

The specific-heat measurements in the temperature interval from 2 to 100 K were carried out using quasiadiabatic calorimeters equipped with commercial Pt and Ge resistors as sample thermometers. Details of the calorimeters have been described earlier.[11–13] For the experiments below 2 K a ^{3}He evaporation cryostat operating in the continuous mode was employed. For the heat-capacity measurements, either a single sample holder, with a commercial Ge resistance thermometer, or a multiple sample holder arrangement having calibrated Speer and RuO_2 resistance thermometers were used. To calculate the specific heat, the nearly adiabatic (isoperibol) drift lines in the heat-capacity curves were fitted to an exponential function as described elsewhere.[14]

III. RESULTS

The measured specific heats $C_P(T)$ are shown in Fig. 3. For clarity we have plotted only the data for three samples, the unsubstituted oxygen-rich compound ($x=0$), a Ga-substituted sample ($x=0.5$), and the oxygen-deficient compound $NdBa_2Cu_3O_{6.2}$. The heat-capacity data of all other Ga-substituted compounds are located between

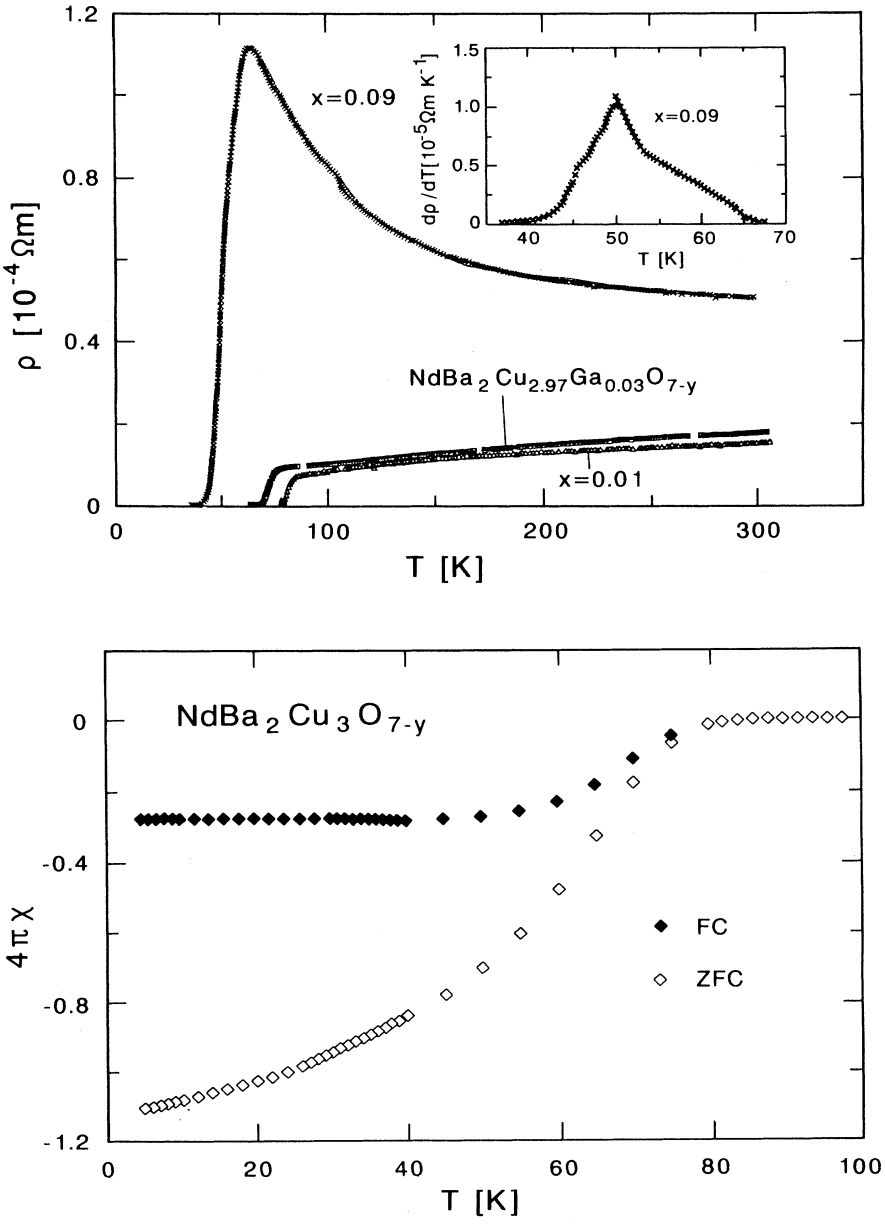

FIG. 2. (a) Temperature dependence of resistivity for three $NdBa_2Cu_{3-x}Ga_xO_{7-y}$ compounds Δ for $x=0.01$, □ for $x=0.03$, ++ for $x=0.09$. The inset shows $d\rho/dT$ vs T for the compound with $x=0.09$. (b) Field-cooled and zero-field-cooled susceptibilities as a function of temperature in a field of 100 G for the unsubstituted, $x=0$ compound.

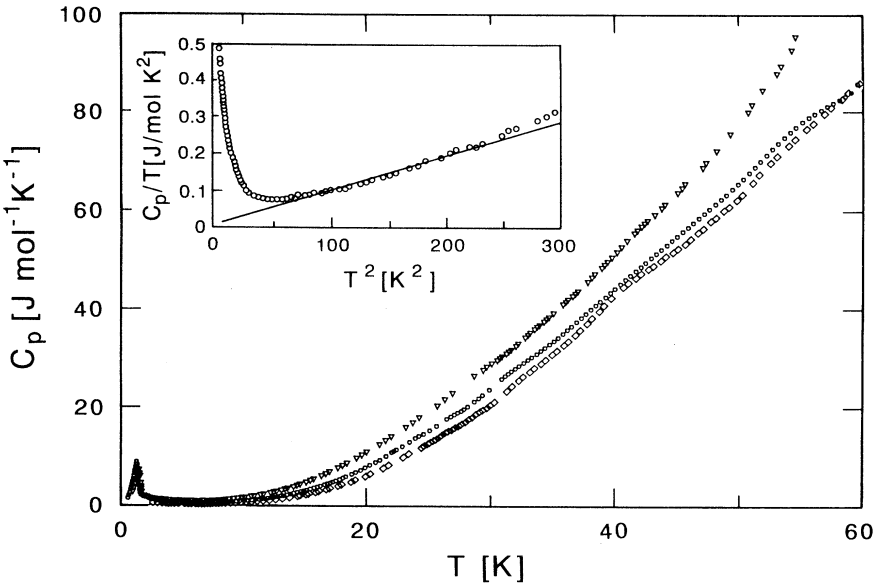

FIG. 3. Specific heat C_P as a function of temperature for the Ga-substituted compositions ◇◇◇ for $x=0$ with $y\approx 0.05$, ▽▽▽ for $x=0$ with $y=0.8$, and ○○○ for $x=0.5$ with $y\approx 0.06$. The inset shows a plot C_P/T vs T^2, for $x=0.5$ with $y\approx 0.06$.

those of the unsubstituted compounds. Sharp peaks occur below 2 K and indicate magnetic ordering of Nd^{3+} ions. The lattice and electronic contributions to the heat capacity have to be subtracted from the total measured heat capacity in order to determine the magnetic specific-heat contribution. An approximate determination of the lattice and the linear contributions to the specific heat was carried out by plotting C_P/T vs T^2, where C_P is the measured specific heat. One such plot is shown as the inset for Fig. 3. The straight-line region between 7 and 15 K is least-squares fitted. From the slope and the intercept, the coefficient of the lattice specific-heat term β and the coefficient of a linear specific-heat term γ were determined. The limiting value of the Debye temperature $\theta_D(0)$ was calculated from $\theta_D(0)=(1944r/\beta)^{1/3}$ where r is the number of atoms present in the compounds. The results are tabulated in Table III.

TABLE III. The linear term γ, lattice term β, and the initial Debye temperature $\theta_D(0)$ values for the specific heats of samples with different Ga concentration x, of $NdBa_2Cu_{3-x}Ga_xO_{7-y}$ obtained from the linear fit of the C_P/T vs T^2 graphs. The estimated error for $\theta_D(0)$ is around 5% and for the linear term is around 10%, except for the sample with $x=0.01$ where the error estimated is as high as 50%.

x (Ga)	Linear term γ (mJ/mol K^2)	Lattice term β (mJ/mol K^4)	$\theta_D(0)$ (K)
0.0	12.09	0.524	364
0.01	142.24	0.578	352
0.03	18.62	0.587	351
0.09	21.34	0.646	339
0.15	9.39	0.667	336
0.30	32.86	0.816	314
0.50	13.91	0.820	312
0.0, $y=0.8$	54.39	1.118	276

A. Schottky anomaly due to crystalline electric-field effects

After subtraction of the lattice and linear terms from the total specific-heat broad anomalies centered around 30–45 K are observed. Theoretical calculation on crystalline electric-field (CEF) effects in Ga-substituted Nd123 compounds by the present authors[10] has been confirmed experimentally by inelastic neutron scattering performed on one of the samples ($x=0.5$, $y\approx 0.8$).[15] These theoretical and experimental results locate the first excited level, due to crystal-field split energy in $NdBa_2Cu_{2.5}Ga_{0.5}O_{6.2}$, at an energy of $\Delta=108\pm 7$ K above the ground level. This value is in good agreement with the value obtained for the unsubstituted sample $NdBa_2Cu_3O_{7-\delta}$.[16] The configuration of the Nd^{3+} ion is obviously not appreciably changed by Ga substitution. The Nd^{3+} ion is a Kramer ion and the ground state as well as the excited state are doubly degenerate. Since the other excited levels occur at much higher temperatures, the effects of CEF can be well described by two levels only. Such a two-level system should be reflected in the specific-heat curve by a Schottky anomaly with a maximum contribution of 3.64 J/mol K expected at a temperature of $T=0.417\times 108$ K.[17] However, the existence of such a contribution could not be verified for the following conditions. According to Fig. 3, the expected additional specific heat represents only about 7% of the measured lattice specific heat and would correspond to a variation of the equivalent Debye temperature of $\Delta\theta_D=20$ K in the vicinity of 40 K. Unfortunately, the detailed structure of lattice heat as given by the real phonon density of states displays a minimum in the curve $\theta_D(T)$ for most solids exactly in the discussed temperature range ($\theta_D/20<T<\theta_D/10$). In addition, the lattice specific heat of our samples depends strongly on the Ga substitution.

In conclusion, from our specific-heat data we are not able to confirm the existence of a Schottky anomaly near

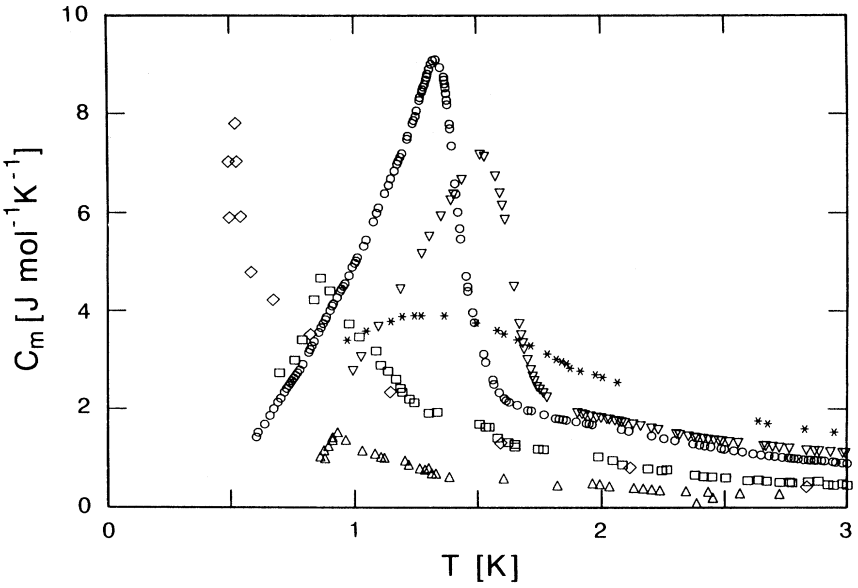

FIG. 4. Temperature variation of magnetic specific heat C_m of $NdBa_2Cu_{3-x}Ga_xO_{7-y}$: ◇◇◇ for $x=0$, △△△ for $x=0.01$, □□□ for $x=0.03$, *** for $x=0.3$, ○○○ for $x=0.5$ with $0.05<y<0.15$, ▽▽▽ for $x=0$ with $y=0.8$.

40 K. On the other hand, we cannot rule out the existence of the same since the temperature dependence of the lattice specific heat can easily mask the expected specific-heat anomaly.

B. Magnetic specific-heat anomalies

The magnetic specific heats at low temperatures, $C_m=C_P-\gamma T-\beta T^3$, for the studied Ga-substituted and nearly oxygen stoichiometric Nd123 compounds are shown in Fig. 4 together with the magnetic specific heat of the unsubstituted superconducting compound $NdBa_2Cu_3O_{6.9}$ as reported in literature.[18] The magnetic specific heat of the oxygen-deficient sample, $NdBa_2Cu_3O_{6.2}$ is also plotted as a function of temperature in Fig. 4 in order to compare directly the influence of Ga substitution and/or oxygen deficiency.

The measured magnetic specific heats C_m, attributed to Nd^{3+}-ion ordering are centered around 1.5 K. The maximum value of the magnetic specific-heat anomalies C_{max} vary between 1.5 J/mol K and nearly 10 J/mol K. These maxima are 2 orders of magnitude larger than the subtracted lattice and linear contributions. Thus the magnetic specific heat is dominant and can be regarded as almost *independent* of the procedure chosen to correct for lattice and linear terms. The sample holder also contributes always less than $\approx 7\%$ to the total measured heat capacity below 4 K. The relative inaccuracies of the deduced magnetic specific heats are estimated to be less than 2% for all the samples.

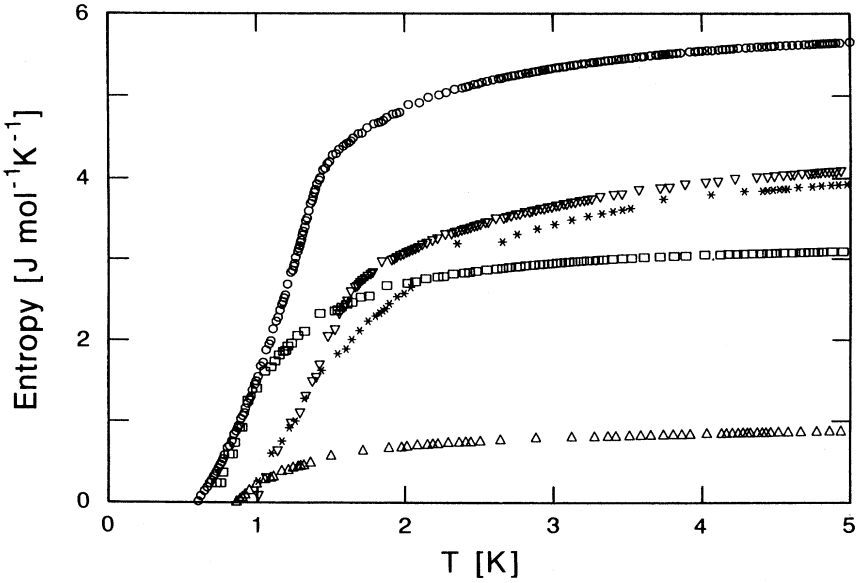

FIG. 5. Magnetic entropy $S_m(T)$ for $NdBa_2Cu_{3-x}Ga_xO_{7-y}$ for $x=0.01$, 0.03, 0.3, 0.5 with $0.05<y<0.15$ and $x=0$ with $y=0.8$ using the same symbols as explained in caption of Fig. 4.

TABLE IV. The characteristic parameters derived from the temperature dependence of the internal energy as well as the entropy, and for comparison that of theoretical values for the different magnetic model systems with different dimensionality (Ref. 28). x denotes the Ga concentration in the compounds, C_m the magnetic specific heat, E_{max} and S_{max} are the magnetic energy and entropy at T_{max}, the temperature at which the maximum of specific heat anomaly occurs. S_∞ represents the saturated magnetic entropy far away from T_{max}.

x (Ga)	C_{max}/R	E_{max}/R	S_{max}/R	$(S_\infty - S_{max})/R$	$(S_\infty - S_{max})/S_\infty$
0.01	0.172	0.016	0.0165	0.0919	5.5872
0.03	0.467	0.096	0.1036	0.2600	2.5097
0.30	0.474	0.144	0.1539	0.3183	2.0681
0.50	1.097	0.325	0.4215	0.2574	0.6108
0.0, $y=0.8$	0.877	0.243	0.2570	0.2373	0.9230
1D Ising				0.6930	
2D Ising			0.3060	0.3870	
3D Heisenberg		0.600	0.4300	0.2600	0.6000
3D Ising		0.220	0.5600	0.1330	0.2375

The temperature at which C_{max} occurs (T_{max}), in the compounds reported here, $NdBa_2Cu_{3-x}Ga_xO_{7-y}$ vary between 0.86 and 1.51 K. The magnetic anomalies display remarkably different shapes (Fig. 4). A very small Ga concentration of $x=0.01$ nearly doubles the magnetic transition temperature from 0.53 K (for the unsubstituted oxygen-rich sample) to 0.93 K. The sharp peak, however, disappears and we observe a rather tiny and smeared out magnetic specific heat. For the compound with $x=0.03$, the Néel temperature occurs at 0.86 K and a peak in the magnetic specific heat which is about three times as large is seen. Both samples are superconducting with transition temperatures of 81.2 and 70.5 K, respectively. The next sample with $x=0.3$ is nonsuperconducting and a large bell-shaped anomaly is associated with the magnetic transition around 1.24 K. For the compound with the maximum Ga concentration reported here, $x=0.5$, a very sharp anomaly is observed at 1.33 K. A similar sharp ordering is detected at 1.51 K for the oxygen-deficient and non-superconducting compound ($x=0$, $y=0.8$) in approximate agreement with an earlier reported value of 1.63 K.[3,5]

From the magnetic specific-heat data, the magnetic entropy $S_m(T)$ as well as the magnetic internal energy $E_m(T)$ were calculated using the equations

$$S_m(T)=\int_0^T \frac{C_m}{T'}dT' ,$$
and
$$E_m(T)=\int_0^T C_m dT' . \quad (1)$$

The temperature dependence of the magnetic entropies for the investigated compounds is shown in Fig. 5. Nearly constant high-temperature values are observed above 5 K. The entropy and magnetic internal energy values at T_{max} are listed in Table IV.

C. Magnetic entropy

The data shown in Fig. 5 indicate a systematic increase of the magnetic entropy above 5 K with increasing concentration of Ga. The total expected entropy associated with the ordering of Nd^{3+} ions is $R\ln 2=5.76$ J/mol K, since it is a Kramer ion with a low-lying ground doublet and the first excited level far away from the ground state at around 100 K.[16] In the calculation of entropy the correction due to the C_m in the temperature range 0–0.45 K is very small (about 0.02% compared to that of the maximum expected entropy) as most of the entropy is derived above the minimum temperature of measurements.

For the low Ga replacement $x=0.01$, $x=0.03$ the magnetic entropies at the Néel temperatures of 0.93 and 0.86 K are only 9 and 27 %, respectively, of the theoretical value for complete ordering of spins. For the compound with $x=0.01$ the magnetic entropy reaches a constant value near 4 K, which is far below the expected entropy of $R\ln 2$. The small entropy achieved below T_{max} as well as the total entropy derived at 4 K in these two cases indicate the presence of short-range rather than a long-range magnetic ordering. There is no longer an increase of the magnetic entropy with temperature at 4 K which suggests that only a small number of spins may participate in the magnetic ordering. In contrast to this situation, for the nonsuperconducting compounds with $x=0.5$, the full entropy expected is reached at 4 K; about 70% of the maximum entropy is achieved below T_{max}. This indicates the presence of long range ordering with isotropic magnetic interaction. The magnetic entropy of other samples lie between these two extreme cases.

The systematic change of entropy of the Ga-substituted Nd123 compounds reported here is similar to that observed in the case of Nd123 compounds with different oxygen concentration.[5] The characteristic parameters are derived from the entropy at various temperatures and are compared with the calculated values for the known magnetic models in Table IV along with the corresponding values for magnetic specific heat and internal energy. The information extracted from these characteristic parameters are utilized for further analysis.

D. Analysis of magnetic ordering of Nd^{3+} ions

1. Nonsuperconducting compounds

(a) $NdBa_2Cu_{2.5}Ga_{0.5}O_{7-y}$ *and* $NdBa_2Cu_3O_{6.2}$. The maximum Ga-substituted, nonsuperconducting sample $NdBa_2Cu_{2.5}Ga_{0.5}O_{7-y}$ and the oxygen-deficient sample are characterized by sharp magnetic transitions as shown in Fig. 4. The entropy derived for both the samples below T_N amounts to approximately $S_m = 0.7R \ln 2$. The expected entropy value of $R \ln 2$ is reached at 4 K for both these compounds indicating the presence of *long-range magnetic ordering* in these compounds.

(b) Determination of coupling constants. The magnetic specific-heat data well below T_N show a T^3 dependence for the maximum Ga-substituted sample $NdBa_2Cu_{2.5}Ga_{0.5}O_{7-y}$ reported here. This T^3 dependence of the magnetic specific heat, well below T_{max}, is used to derive the magnetic interaction strength in this compound. This is depicted as a graph of C_m vs T^3 in Fig. 6. This clearly shows that the magnetic ordering is of antiferromagnetic and of three dimensional in nature. The experimental data is least-squares fitted in the temperature range from 0.45 to 0.8 K. The coupling constant J, then is obtained from[19]

$$C_m = 13.7R \left[\frac{k_B T}{12JS} \right]^3 , \tag{2}$$

where S denotes the spin state of the magnetic ion, R is the gas constant, and k_B is the Boltzmann constant. The coupling constant is $J \approx 0.48$ K.

A second way of determining the coupling constant is from the magnetic internal energy of the system sufficiently far away from the T_N. The internal energy is calculated using Eq. (1) at 4 K. From this value the coupling constant is calculated using

$$\frac{E_m}{R} = S^2 q \frac{J}{k_B} \left[1 + \frac{\Gamma}{qS} \right] , \tag{3}$$

where q is the number of nearest neighbors. Here, Γ is 0.67 for the simple-cubic case, where $q = 6$. The coupling constant calculated from the internal energy yields $J \approx 0.53$ K.

The coupling constant can also be estimated from the high-temperature tail of the magnetic specific heat far away from the T_N. In this region, even the presence of negligibly small quantity of the linear term may hinder detailed analysis. Hence such analysis was not carried out.

Finally, the coupling constant is indirectly related to the position of the Néel temperature T_N. Using an equation by Rushbrooke and Wood[20] we can estimate the coupling constant from the following formula:[21]

$$T_N = 1.65 \left[1 + \frac{0.67}{qS(S+1)} \right] \frac{J}{k_B} . \tag{4}$$

The derived coupling constant yields a value higher than those calculated with the two former methods, $J \approx 0.7$ K.

The coupling constants obtained from the first two standard methods agree quite well. The averaged value yields $J \approx 0.54$ K for $NdBa_2Cu_{2.5}Ga_{0.5}O_{7-y}$. The Néel temperature of $NdBa_2Cu_{2.5}Ga_{0.5}O_{7-y}$ viz. 1.33 K, is lower compared to the Néel temperature of pure oxygen-deficient sample $NdBa_2Cu_3O_{6.2}$. This result will be confirmed and become understandable in the following section. We note that from the above calculations no information on the anisotropy of the coupling in the *a*, *b*, or in *c* direction could be gained. For that single crystals are required. We conclude that the Ga-substituted ($x = 0.5$, $y \approx 0.06$) sample exhibits three-dimensional ordering characteristics.

(c) $NdBa_2Cu_{2.7}Ga_{0.3}O_{7-y}$. *For* this nonsuperconducting compound we assume that the bell-shaped broad maxima near 1.24 K is associated with magnetic ordering rather than with a Schottky anomaly of unknown origin. The temperature dependence of the specific-heat curve is not consistent with a Schottky-type specific-heat anomaly. In contrast, the curve is well described by the specific heat of a two-dimensional (2D) Ising model.[22] The fit to the experimental curve is shown in Fig. 7(a). The Néel temperature obtained from the fit is 0.685 K. The corresponding coupling constants for the *b* and *a* directions are $J_1 = 1.55$ K and $J_2 = 0.0074$ K. In conclusion, the relatively highly Ga-substituted or deoxygenated nonsuperconducting samples exhibit highly anisotropic 2D Ising-type magnetism compared to the 3D ordering of the former.

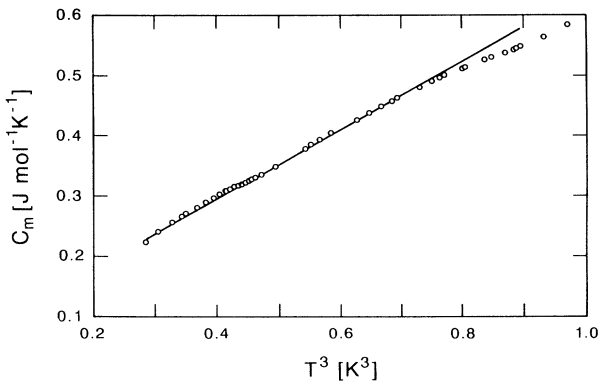

FIG. 6. Graph drawn for the computation of coupling constants for $NdBa_2Cu_{2.5}Ga_{0.5}O_{7-y}$: C_m vs T^3 plot with the least fit in the temperature interval from 0.45 to 0.8 K.

2. Superconducting compounds

(a) $NdBa_2Cu_{2.99}Ga_{0.01}O_{7-y}$ *and* $NdBa_2Cu_{2.97}Ga_{0.03}O_{7-y}$. It is surprising that a very small concentration of Ga, $x = 0.01$ and 0.03, produces such a dramatic shift of the magnetic ordering temperature from 0.53 K for the unsubstituted stoichiometric compound to 0.93 and 0.86 K, respectively. An equally sudden drop of the superconducting transition temperature is observed, from 89.7 to 81.2 and 70.5 K (see Table I). The magnetic anomalies, although much less pronounced in comparison to that of the nonsuperconducting compounds dis-

cussed earlier, are relatively sharp and symmetric around the T_{max} for both compounds. A modeling by 2D Ising parameters fails but the magnetic specific heat can be described reasonably well for both samples with a 1D Ising model.

More detailed examination reveals that the 1D Ising model[23] is only one of the known mathematical representations for the temperature dependence of the magnetic specific heat, but only when the number of participating spins is substantially reduced, namely to 9% for the $x=0.01$ sample and to 27% for the $x=0.03$ sample. Then the theoretical curve (for 1D Ising) multiplied with 0.09 or 0.27, respectively, fits the experimental data. For the sample $x=0.03$, the experimental results are plotted in Fig. 7(b) together with the fit curve for the 1D Ising model where only 27% of the spins are considered. The critical parameters for the two compounds $T_{max}=0.6$ and 0.5 K, and coupling constants $J\approx 1.18$ and 1.0 K, respectively, are listed in Table V. It remains an open question whether the 1D Ising model is the only possible modeling. Recently, Allenspach presented calculation of magnetic clusters with short correlation length (20 Å)

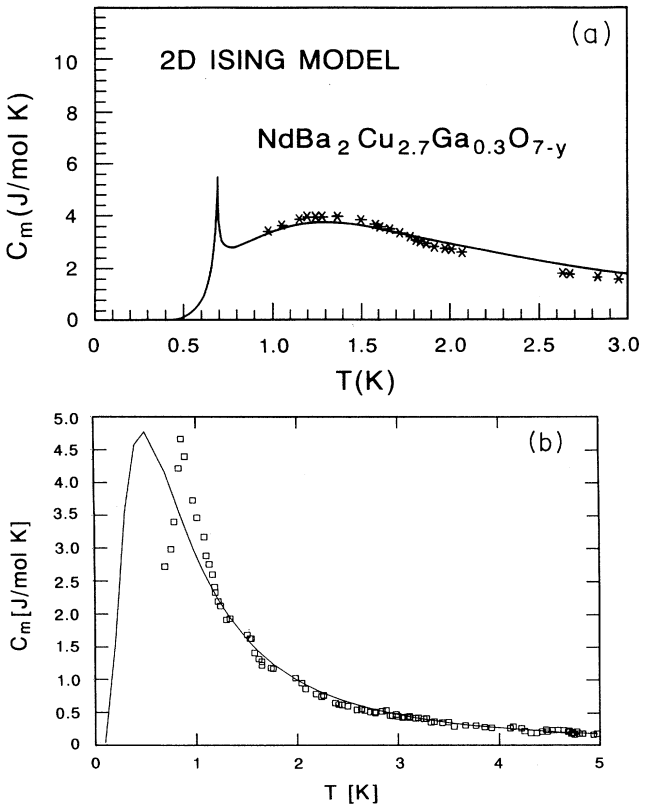

FIG. 7. Fit of magnetic specific heat C_m to Ising models. (a) $C_m(T)$ for $NdBa_2Cu_{2.7}Ga_{0.3}O_{7-y}$ with the fit corresponding to exact solution of the 2D anisotropic Ising model: ***, experimental data; ——, 2D anisotropic Ising model fit with $T_N=0.685$ K and $J_1=1.55$ K and $J_2=0.0074$ K. (b) $C_m(T)$ for $NdBa_2Cu_{2.97}Ga_{0.03}O_{7-y}$ with the theoretical fit of the 1D Ising model. □□□, experimental data; —— fit corresponding to the 1D Ising model with $J=1$ K.

TABLE V. T_{max} and coupling constants have been determined for different Ga concentration. Coupling constant of the unsubstituted compound, $x=0$, is included for comparison as reported by Lee (Ref. 5). T_{max} (expt.) is the experimental data whereas T_{max} (fit) is the T_{max} derived from the fit.

x (Ga)	T_{max} (expt.) (K)	T_{max} (fit) (K)	J_1 (K)	J_2 (K)	Magnetic model
0	0.53	0.52	0.85	0.017	2D Ising
0.01	0.93	0.6	1.18		1D Ising
0.03	0.86	0.5	1		1D Ising
0.3	1.24	0.685	1.55	0.0074	2D Ising
0.5	1.33	1.297	0.54		3D

showing that, in the case of $NdBa_2Cu_3O_{7-\delta}$ $(0<y<0.1)$ the specific heat is neither of 1D Ising nor of 2D Ising or Heisenberg type, but could be explained by 2D Heisenberg spin clusters.[24] We summarize, the magnetic transition temperature as well as the coupling strength increase with increasing Ga concentration. We have to assume that not the entire spin system is involved in magnetic ordering for the compounds having low Ga content. Introduction of an seemingly insignificant amount of Ga or a rather small oxygen understoichiometry transforms an initially unsubstituted and nearly stoichiometric $NdBa_2Cu_3O_{7-\delta}$ sample with 2D Ising-type magnetism to a magnetically weakened 1D Ising system with reduced number of involved spins or breaks the magnetic structures into clusters.

IV. DISCUSSION

The experimental results described in the earlier sections have a striking similarity with those of the unsubstituted compound with different oxygen concentrations.[18] With different Ga content, the magnetic ordering varies from one dimensional to two dimensional and then to three dimensional. There exists a clear correlation between the existence of low-dimensional magnetism (in compounds with low Ga contents) and superconductivity. There also exists an inverse correlation between T_{max} (temperature at which the specific-heat maximum occurs) and T_c. The temperatures T_{max} and T_c as a function of the Ga concentration in $NdBa_2Cu_{3-x}Ga_xO_{7-y}$ and as a function of the oxygen content in $NdBa_2Cu_3O_{7-\delta}$ are shown in Fig. 8. This figure facilitates a comparison between the behavior of the Ga-substituted compounds and the unsubstituted compounds with different oxygen concentrations. We observe a steep increase of the T_{max} and in turn an increase in the strength of the magnetic interaction between the Nd^{3+} ions and a corresponding decrease in T_c as a function of Ga concentration x. The variation of T_{max} and T_c are larger than those in the case of the unsubstituted compounds with different oxygen contents, $dT_{max}/dx=0.4$ K/at.% of Ga and $dT_c/dx=12$ K/at.% of Ga, whereas $dT_{max}/dy=0.3$ K/at.% of oxygen and $dT_c/dy=8$ K/at.% of oxygen (considering only chain oxygen).

The initial steep increase of T_{max} may be related to a decrease in the hole concentration due to the Ga substitu-

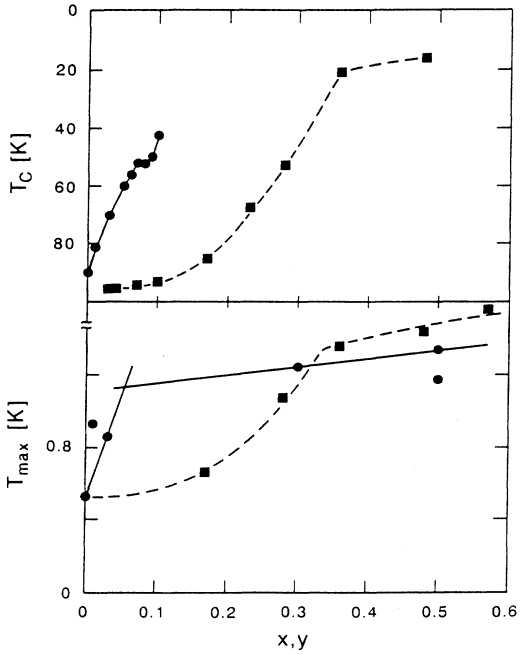

FIG. 8. Variation of T_{max} and the variation of superconducting transition temperature T_c as a function of Ga concentration in $NdBa_2Cu_{3-x}Ga_xO_{7-y}$ and of the oxygen reduction in unsubstituted compounds: ■■■, for Ga-substituted compounds; ●●●, for oxygen-depleted compounds.

tion at the Cu sites. The magnetic ordering of Nd^{3+} ions in these compounds cannot be dipolar. As the number of charge carriers in these compounds is 2 orders of magnitude less than that in metals, the probable mechanism would be superexchange rather than indirect exchange of the RKKY type. Ordering of Nd^{3+} ions in $NdBa_2Cu_3O_{6.9}$ is reported to be of 2D Ising type with large anisotropy, i.e., $J_1/J_2 > 50$.[5] With the substitution of Cu by Ga, the magnetic ordering becomes 1D Ising-like. The neutron-diffraction data on the $NdBa_2Cu_3O_{7-\delta}$ with different oxygen content y shows a remarkable increase in the Nd-O bond distances along the a direction and a decrease along the b direction, which is an effect of the hole depletion.[25] A similar change in the Nd-O distances along different directions in the Ga-substituted compounds may result in an increase in the anisotropy of magnetic interaction driving the system to 1D Ising-like. According to the entropy results, the spins involved in such an interaction, however, are only 9 and 27% in $x=0.01$ and 0.03. This situation can also be pictured in terms of spin clusters as has been reported by Allenspach *et al.* in the case of $DyBa_2Cu_3O_{7-y}$ compound.[24] In Fig. 8, it is seen that the increase of T_{max} after the O-T transition and in the nonsuperconducting regime is not so steep as in the initial stages of Ga substituting. This suggests that a decrease in the hole concentration cannot be the only mechanism involved. Another mechanism involved may be the ordering of Cu ions in the CuO_2 planes.[26] The Cu ions order only in the nonsuperconducting compounds and they are known to order along the ab plane.[27] As the Cu ions order along the ab plane, the ordering of Nd^{3+} ions may be facilitated through the Cu-ion ordering along the ab plane leading to the development of long-range ordering with the increased Ga content. This may explain the restoration of long-range order from 1D to 2D and then to (isotropic) 3D. The increase of the dimensionality of the interaction from 1D to 2D and then to 3D is also depicted by the systematic increase of entropy with increase of Ga concentration. Comparing $NdBa_2Cu_3O_{6.2}$ and $NdBa_2Cu_{2.5}Ga_{0.5}O_{7-y}$, the ordering temperature of Nd^{3+} ions in the Ga-substituted compound is lower (1.33 K) than in the former (1.51 K). This decrease can be attributed to the overall expansion of the lattice with the replacement of Cu by Ga.

V. CONCLUSION

Summarizing, the effects of charge carrier density on the magnetic ordering of Nd^{3+} ion is stronger than for the other high-temperature oxide superconductors, for example, Dy or Er. Our experimental results point out that the decrease in the carrier concentration via depletion of the oxygen ions and the Ga concentration have very similar effects on the magnetic properties of the Nd^{3+} ions whereby the Ga is more effective in decreasing T_c and increasing T_{max}. A combined influence is registered of (i) reduction of the hole concentration in the ab planes and, as a consequence, an increase in superexchange interaction in the a axis and decrease of the same in the b axis leading to a strong anisotropy in the Nd-Nd interaction, (ii) gradually increasing magnetic ordering of the Cu spins, when the unsubstituted compound $NdBa_2Cu_3O_{7-\delta}$ is substituted with Ga and/or O vacancies facilitating the long-range ordering. The interesting range of very low Ga substituting, $x<0.1$ is further investigated. It constitutes a model system to study the transition from 2D to 1D Ising systems and the influence of magnetic field on the ordering phenomena.

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