Magnetic susceptibility, specific heat, and crystal-field effects in neodymium cuprate superconductors

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(Received 17 February 1995; revised manuscript received 15 May 1995)

We report here the results of magnetic susceptibility of both *n*- and *p*-type superconductors, $Nd_{2-x}Ce_xCuO_{4-y}$ (x = 0.14, 0.15, 0.16, and 0.18) and $NdBa_2Cu_{3-z}Zn_zO_{7-\delta}$ (z = 0 and 0.02) in the temperature range 2 to 300 K and specific heat measurements on *p*-type superconductors in the temperature range $5 \le T \le 300$ K. Crystal-field (CF) analysis of these results has been performed considering *J* mixing of the lowest eleven multiplets with intermediate-coupled wave functions. The CF analysis of the magnetic susceptibility data is consistent also with the reported inelastic neutron-scattering spectra. The specific heat data have been accounted for by considering Debye, Einstein, and Schottky contributions.

I. INTRODUCTION

The cuprate superconductors $Nd_{2-x}Ce_{x}CuO_{4-y}$ (NCCO) and NdBa₂Cu₃O_{7- δ} (NBCO) form an interesting series of compounds due to possible interplay between superconductivity and magnetism. The NCCO system has the unique feature of exhibiting superconductivity for small concentrations of cerium (0.14 $\leq x \leq$ 0.18) which replaces neodymium. Hall-effect and thermoelectric power measurements indicate that the prime carriers are electrons in these systems and in view of this, these materials are particularly significant and distinct from the other high-temperature cuprate superconductors. These compounds have superconducting transition temperatures (T_c) around 24 K. Besides, these compounds have the simplest crystal structure of all the cuprate superconductors with planar Cu-O layers and no apical oxygen, perhaps making them the most fundamental of the hightemperature superconductors. The NBCO system, on the other hand, belongs to a class of superconductors with high T_c (90 K). The dominant charge carriers in this system are holes rather than electrons and the basic structure consists of Cu-O planes with apical oxygen in contrast to the *n*-type superconductors. The rate of T_c suppression in NBCO due to the substitution of a nonmagnetic 3d element such as zinc at the copper site is larger than in the $YBa_2Cu_3O_{7-\delta}$ system.¹ These facts have led to a lot of interest in the study of these superconductors.

Earlier studies on NCCO systems include structural analysis, measurements of inelastic neutron-scattering (INS) spectra, magnetic susceptibility, and specific heat measurements. X-ray-diffraction measurements have been conducted and diffraction peaks were indexed which showed a tetragonal structure. The lattice parameters containing different amounts of cerium ions have also been determined.² X-ray diffraction (XRD) and x-ray photoemission spectroscopy measurements³ revealed structural anomalies in NCCO. Near x=0.15 drastic decreases in the Nd-O(1) and Cu-Nd bond lengths and unit-cell volume have been found and attributed to rapid electron transfer to the CuO₂ layers from the Nd(Ce) layers. X-ray powder diffraction has also been used to determine the average ionic radius of the cerium present in the system. The effective valence of cerium has also been calculated. The decrease in both the *c*-lattice dimension and the unit-cell volume with increasing *x* suggested the presence of Ce⁴⁺ rather than Ce³⁺ (Refs. 4 and 5). INS experiments have been conducted on the systems Nd₂CuO₄ and Nd_{1.85}Ce_{0.15}CuO_{4-y} and the crystal-field (CF) transitions have been determined.⁶⁻¹¹ Magnetic susceptibility measurements have been performed on both polycrystal-line¹²⁻¹⁴ and single-crystal^{15,16} samples. Heat-capacity measurements on parent and doped compounds showed antiferromagnetic ordering of the Nd moments for Nd₂CuO₄ and Nd_{1.85}Ce_{0.15}CuO_{4-y} at 1.7 and 1.2 K, respectively.¹⁷

Likewise XRD measurements, INS spectra, magnetic susceptibility, and specific heat measurements were per-formed also on the NBCO system. $^{18-29}$ X-ray-diffraction measurements revealed an orthorhombic structure and the lattice parameters were determined.^{18,19} Inelastic neutron-scattering measurements have been conducted by a number of groups and CF levels have been found.²⁰⁻²⁴ Magnetic susceptibility measurements show a clear deviation from the Curie-Weiss law for NBCO which has been attributed to CF effects.^{21,25,26} Specific heat measurements have been performed on polycrystalline NBCO and specific heat data below T_c are accounted for by both Debye and Einstein lattice contributions and a Schottky contribution from CF effects.^{23,27} The magnetic ordering temperature of Nd³⁺ in this system has been found to be around 0.52 K from specific heat measurements.^{28,29} The effect of substitution of zinc at the copper site for the NBCO system has been investigated. The XRD pattern¹ shows the formation of single phase for $0 \le x \le 0.8$. Variations of lattice parameters, degree of orthorhombicity, unit-cell volume, and oxygen content as functions of z for the NdBa₂Cu_{3-z}Zn_zO_{7- δ} system have been determined.¹

Motivated by the fact that in NCCO the magnetic ion is situated above and below the Cu-O planes in contrast

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to the NBCO system and that the crystal-field splittings in NCCO are small compared to the NBCO system we aimed at a systematic study on the magnetic and thermal properties of $Nd_{2-x}Ce_xCuO_{4-y}$ with various cerium concentrations and zinc-doped NBCO. Also the crystal field acts as a local probe at the rare-earth site and it would therefore be interesting to make a systematic analysis of our magnetic susceptibility data in order to study the variation of the CF parameters with changes in symmetries and doping at the rare-earth as well as copper site and to compare and correlate our analysis to the results of measurements of other physical properties. Even though magnetic susceptibility and specific heat data have been published before, the proposed method of analysis viz., beginning with the CF parameters derived from INS results and extending the model to include Jmixing in order to obtain a close fit to magnetic susceptibility and specific heat data, is expected to provide additional insight and useful information on the possible interaction between superconductivity and 4f magnetism in these compounds.

II. EXPERIMENTAL DETAILS

The $Nd_{2-x}Ce_xCuO_{4-y}$ (x=0.14, 0.15, 0.16, and 0.18) compounds were synthesized by high-temperature solidstate reaction.³⁰ The as-prepared compounds did not exhibit superconductivity down to the lowest measured temperature. Superconductivity was induced by reducing the as-prepared samples in a continuous vacuum of $\simeq 10^{-5}$ mbar at 850 °C for 6 h. NdBa₂Cu_{3-z}Zn_zO₇₋₆, (z=0 and 0.02) compounds were also prepared by standard solid-state reaction.¹ NCCO and zinc-doped NBCO samples were characterized by XRD, electrical resistivity, and magnetic susceptibility measurements. X-ray powder-diffraction patterns of NCCO and NBCO samples revealed the single phase nature of the compounds with tetragonal and orthorhombic structures, respectively.^{30,1} Superconductivity was observed in NCCO samples with onset of superconducting transition around 24 K in electrical resistivity measurements.³⁰ The asprepared sample of x=0.16 which is a nonsuperconductor (ns) has also been included in the present study for comparison purposes. The superconducting transition temperatures are 85 and 67 K for the parent and zincdoped NBCO compounds,¹ respectively.

dc magnetic susceptibility measurements have been carried out in a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer in the temperature range 2 to 300 K in a magnetic field of 100 and 2000 G for NCCO and NBCO, respectively, in the normal state. Figures 1 and 2 show the temperature variation of the susceptibility for these compounds.

Heat-capacity measurements have been performed on NdBa₂Cu₃O_{7- δ} and NdBa₂Cu_{2.98}Zn_{0.02}O_{7- δ} using an automated quasiadiabatic calorimeter. The details of the calorimeter are described elsewhere.³¹ The calibration of the experimental setup was checked using a Nb pellet which exhibits superconductivity around 9 K. The values of the electronic heat-capacity coefficient (γ) and Debye temperature (Θ_D) derived from a linear fit of



FIG. 1. Magnetic susceptibility of (a) superconducting $Nd_{1.85}Ce_{0.15}Cu_{4-y}$ and (b) nonsuperconducting $Nd_{1.84}Ce_{0.15}Cu_{4-y}$ (*) experimental; (---) present fit; (----) fit due to Ref. 16.

 C_p/T versus T^2 data between 10 to 20 K were found to be in good agreement with those reported in the literature.³² The results of heat-capacity measurements of these samples are shown in Figs. 3 and 4.

The magnetic susceptibility data both for NBCO and NCCO above T_c were initially fitted to an expression of the form



FIG. 2. Magnetic susceptibility of NdBa₂Cu_{3-z}Zn_zO_{7- δ} (*) and (+) are experimental $\bar{\chi}$ for z=0 and z=0.02, respectively. (-.-.) and (---) are calculated $\bar{\chi}$ for z=0 and z=0.02, respectively. (----) calculated $\bar{\chi}$ of z=0 as in Ref. 20.



FIG. 3. Specific heat of $NdBa_2Cu_3O_{7-\delta}$. (•) experimental, (---) Debye and electronic contributions; (----) Einstein contribution; (----) Schottky contribution; (----) total contribution due to Debye, electronic, Einstein, and Schottky. Inset: Measured specific heat.

$$\chi = \chi_0 + \frac{C}{T - \theta_p}$$

and the parameters C, θ_p , and χ_0 given in Table I are found to be close to those reported in the literature.^{16,26} The effective magnetic moments obtained from the above fit have also been included in the same table and are found to decrease with cerium concentration for superconducting samples. Hence CF analysis was undertaken in order to account for the measured magnetic susceptibilities.

III. THEORETICAL BACKGROUND

In the case of Nd^{3+} in NCCO and NBCO, the intramultiplet splitting ranges from 800 to 1000 cm⁻¹ and



FIG. 4. Specific heat of $NdBa_2Cu_{3-z}Zn_zO_{7-\delta}$. (•) experimental, (---) Debye and electronic contributions; (----) Einstein contribution; (----) Schottky contribution; (----) total contribution due to Debye, electronic, Einstein, and Schottky. Inset: Measured specific heat.

the next higher multiplet,³³ i.e., ${}^{4}I_{11/2}$ is only around 1800 cm⁻¹ above the ground term, i.e., ${}^{4}I_{9/2}$. Hence it was necessary to consider J mixing of the multiplet scheme. Further it was found that improved results could be obtained by considering the multiplets higher than ${}^{4}I$ multiplets. Therefore in our analysis we have taken into account J mixing of the first 11 J multiplets and intermediate-coupled wave functions. Structural analysis of these compounds revealed I4/mmm space group with D_{4h} site symmetry¹¹ for NCCO and *Pmmm* space group with D_{2h} site symmetry²¹ for NBCO systems. The crystal-field Hamiltonian, H_{CF} considering orthorhombic symmetry at the rare-earth (Nd³⁺) site in NBCO is of the form

$$H_{\rm CF} = B_2^0 V_2^0 + B_2^2 (V_2^2 + V_2^{-2}) + B_4^0 V_4^0 + B_4^2 (V_4^2 + V_4^{-2}) + B_4^4 (V_4^4 + V_4^{-4}) + B_6^0 V_6^0 + B_6^2 (V_6^2 + V_6^{-2}) + B_6^4 (V_6^4 + V_6^{-4}) + B_6^6 (V_6^6 + V_6^{-6})$$

and the tetragonal symmetry at the Nd^{3+} site in NCCO gives rise to the Hamiltonian

$$H_{\rm CF} = B_2^0 V_2^0 + B_4^0 V_4^0 + B_4^4 (V_4^4 + V_4^{-4})$$
$$B_6^0 V_6^0 + B_6^4 (V_6^4 + V_6^{-4})$$

where B's are the crystal-field parameters and V's are the *n*-particle unit irreducible spherical tensor operators.

The software for calculations of the matrix elements for the form of the Hamiltonian $(H_{\rm CF})$ chosen, determination of the energy eigenvalues and the corresponding eigenfunctions, and the subsequent calculation of the magnetic susceptibility with temperature variation has been developed in the present work. During the calculation of the matrix elements with respect to states characterized by quantum numbers $|SLJM\rangle$, use is made of the Wigner-Eckart theorem wherein the matrix elements take the form

$$\langle Jm | V_k^g | J'm' \rangle = (-1)^{J-m} \begin{pmatrix} J & k & J' \\ -m & q & m' \end{pmatrix}$$

$$\times (-1)^{S+k+J+L'} \sqrt{(2J+1)(2J'+1)}$$

$$\times \begin{cases} L & J & S \\ J' & L' & k \end{cases} \langle SL | \|V_k\| | SL' \rangle ,$$

where the second factor in the equation is the 3j symbol and gives the dependence of an irreducible tensor of rank k on m, m', and J. The factor after the square root represents a 6j symbol and the last doubly reduced matrix element is typical of each multiplet.³⁴ The doubly reduced matrix elements consist of complicated summations over coefficients of fractional parentage of a particular multiplet level. Group-theoretical relationships reported by Judd³⁵ were used in the present case to determine them. The numerical computation of the Clebsch-Gordon coefficients and the Racah coefficients involved in the 3j and the 6j symbols, respectively, was carried out using generalized hypergeometric functions.³⁶ The matrix thus computed was then diagonalized to obtain the energy eigenvalues and the corresponding eigenfunctions.

Composition	$\frac{C}{(\text{emu K/mol Nd}^{3+})}$	θ_p (K)	$\frac{P_{\rm eff}}{(\mu_B/{\rm Nd}^{3+})}$	χ_0 (emu/mol Nd ³⁺)	
x					
0.14	1.49	-41.2	3.46	4.79×10^{-4}	
0.15	1.48	-43.0	3.44	4.82×10^{-4}	
0.16	1.29	-38.0	3.21	4.32×10^{-4}	
0.16(ns)	1.11	-23.0	2.97	7.79×10^{-4}	
0.18(ns)	1.32	-48.0	3.25	1.00×10^{-3}	
z					
0	1.22	-29.2	3.13	1.30×10^{-3}	
0.02	1.08	-23.0	2.94	2.10×10^{-3}	

TABLE I. Fitted free-ion parameters for $Nd_{2-x}Ce_xCuO_{4-y}$ and $NdBa_2Cu_{3-z}Zn_zO_{7-\delta}$.

The diagonalization procedure involved the method originated by Jacobi.³⁷ The temperature variation of the powder magnetic susceptibility was calculated using the Van Vleck formula

$$\chi = \frac{g_J^2 N \mu_{\beta}^2}{2} \sum_i \left[\frac{E_i^{(1)^2}}{k_B T} - 2E_i^{(2)} \right] \exp\left[\frac{-E_i^{(0)}}{k_B T} \right],$$

where $E_i^{(0)}$, $E_i^{(1)}$, $E_i^{(2)}$ are the zeroth, first- and secondorder perturbed Zeeman energies and the other symbols have their usual meaning.³⁸

IV. RESULTS

A. Magnetic susceptibility

At the outset the crystal-field parameters (CFP) for NCCO and NBCO reported in earlier work^{7,20} on fitting the INS spectrum were taken as starting parameters for the fits. It was found that although these CFP could reproduce the INS data well, there were appreciable discrepancies between the calculated and experimental magnetic susceptibility $(\bar{\chi})$ data. We next attempted better fits of our data $(\bar{\chi})$ on all the compounds by studying the effect of each of the CF parameters on $\bar{\chi}$ and CF levels. It may be remarked that the value of B_2^0 was crucial in determining the absolute value of $\overline{\chi}$ above 250 K. At the same time this parameter played a vital role in adjusting the first CF level. B_4^0 was varied so as to get a close fit to the rate of increase of $\overline{\chi}$ on lowering of temperature. B_6^0 was a very effective parameter as the slope of the calculated $\bar{\chi}$ curve could be adjusted to some extent on its variation. The tetragonal parameters had little effect both on the energy levels as well as $\overline{\chi}$ values.

Preliminary tentative fitting of our magnetic susceptibility data was done by considering only the ${}^{4}I$ multiplets. It may be mentioned here that our previous report³⁹ on the NCCO system considering a CF analysis with only the ${}^{4}I$ multiplets gave CFP which had to be considerably modified by inclusion of higher multiplets. However, upon including higher multiplets, an improvement in the fit to the data was obtained, hence J mixing was absolutely necessary so as to get the correct CF levels. For example, for the Nd_{1.85}Ce_{0.15}CuO_{4-y} system when CF calculations were made with only the ground multiplet, (${}^{4}I_{9/2}$) considering the present set of parameters, the calculated energy eigenvalues were found to be 0, 12.2, 27.4, 32.4, and 92 meV. The same CF calculation when repeated with the ⁴*I* multiplets gave the energy eigenvalues as 0, 11.4, 20.2, 26.8, and 91.7 meV. Calculations made with the first eleven multiplets gave values of 0, 12.7, 20.3, 26.6, and 93.5 meV whereas the observed values from INS are 0, 12.2, 20.3, 26.5, and 93.2 meV.⁶ The addition of higher-energy multiplets did not improve the results. From this it is evident that *J* mixing was absolutely essential for a closer agreement between INS and susceptibility data.

The CFP obtained for NBCO and NCCO compounds studied in the present work are presented in Table II and the calculated magnetic susceptibilities are shown in Figs. 1 and 2. The energy eigenvalues and the corresponding eigenfunctions for $Nd_{1.85}Ce_{0.15}CuO_{4-\nu}$ are given in Table III. The energy-level diagram of five distinct Kramers doublets for Nd³⁺ ion in NCCO and NBCO is shown in Fig. 5. The energy-level scheme obtained from INS measurements on $NdBa_2Cu_3O_{7-\delta}$ (Ref. 21) and $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ (Ref. 7) systems are also included in the energy-level diagram. From Figs. 1, 2, and 5 it is evident that the present work not only explains the temperature dependence of $\overline{\chi}$ values reasonably well but also the INS data closely. Also the present set of eigenfunction coefficients for $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ (Table III) are in agreement with those reported earlier.⁴⁰ Inspection of Table II shows that in the case of $Nd_{2-x}Ce_{x}CuO_{4-y}$ it was not necessary to vary the tetragonal parameters (B_4^4) and B_6^4) for fitting the $\bar{\chi}$ for various compositions. Systematic variation of B_2^0 , B_4^0 , and B_6^0 was sufficient to fit the \overline{Y} data of the compounds reported in the present work. A plot of CFP as a function of concentration has been presented in Fig. 6 and discussed in Sec. V.

B. Specific heat

Figures 3 and 4 show the molar heat capacity of $NdBa_2Cu_3O_{7-\delta}$ and $NdBa_2Cu_{2.98}Zn_{0.02}O_{7-\delta}$. The value of the specific heat jump ΔC_p at T_c was found to be 58 mJ/mol K² for NdBa₂Cu₃O_{7-\delta} whereas in the case of zinc-doped NBCO such a jump could not be observed. A least-squares fit of the experimental C_p data of NBCO in the temperature range between 5 and 10 K to the equation

Composition	B ⁰ ₂	B ² ₂	B ⁰ ₄	B_{4}^{2}	B ⁴ ₄	B_{6}^{0}	B_{6}^{2}	B ⁴ ₆	B ⁶ ₆
Z									
0 (Ref. 20)	- 570	-203	- 3060	13	1883	-793	343	-2527	-106
0	-752	471	-2982	-116	1788	-786	256	-2557	-142
0.02	-560	150	-2920	-100	1905	-803	343	-2607	- 106
x									
0.15 (Ref. 7)	-298	0	-2612	0	2002	-618	0	-1805	0
0.14	980	0	-2850	0	1598	-135	0	- 1890	0
0.15	960	0	-2840	0	1598	-105	0	-1890	0
0.16	1005	0	-2625	0	1598	-6 0	0		0
0.16(ns)	795	0		0	1598	- 55	0		0
0.18(ns)	804	0	- 3006	0	1598	-60	0	-1890	0

TABLE II. Crystal-field parameters in cm⁻¹ for NdBa₂Cu_{3-z}Zn_zO_{7- δ} and Nd_{2-x}Ce_xCuO_{4-y}.

$$\frac{C_p}{T} = \gamma + \beta T^2$$

yielded a value of 8.1 mJ/mol K² for γ , the electronic heat-capacity coefficient and 0.585 mJ/mol K⁴ for β . From the value of β the Debye temperature was calculated to be 351 K. A similar analysis for the zinc-doped system gave values of 9.9 mJ/mol K² for γ and 0.509 mJ/mol K⁴ for β . The Debye temperature corresponding to this β was found to be 367 K.

To explain our experimental data on specific heat of $NdBa_2Cu_3O_{7-\delta}$ and $NdBa_2Cu_{2.98}Zn_{0.02}O_{7-\delta}$, we considered the various components that add up to give the total specific heat. First, a mass correction was made to the nonmagnetic $YBa_2Cu_3O_{7-\delta}$ system in order to calculate the Debye temperature for the above two systems. The Debye temperature, θ_D , after the mass correction was calculated to be 361 K. Using this information it was possible to determine the Debye contribution to the total specific heat using the Debye integral.⁴¹ The specific heat data deviate from the Debye approximation for temperatures greater than 10 and 14 K for z=0 and z=0.02 compounds, respectively, suggesting the presence of optical-phonon modes. Hence an Einstein term was included to account for the deviation. It may be mentioned here that the fit to our susceptibility data involved two closely spaced CF levels which are consistent with INS data. We therefore included a Schottky contribution to explain the total measured specific heat. The specific heat data in the temperature range 5 to 50 K could be fitted well to the following equation:

$$C_{p} = \gamma T + \frac{9rR}{x^{3}} \int_{0}^{x} \frac{x^{4}e^{x}dx}{(e^{x}-1)^{2}} + \frac{N_{E}Ry^{2}e^{y}}{(e^{y}-1)^{2}} + C_{\text{Sch}}$$

where the first, second, third, and fourth terms represent the electronic, Debye, Einstein, and Schottky contributions, respectively, and r is the number of atoms present in the molecule, R is the universal gas constant, $x = \theta_D / T$, N_E is the number of degrees of freedom, $y = \theta_E / T$ and θ_E is the Einstein temperature. The Schottky contribution was calculated from the fitted CF levels. Results for NBCO and zinc-doped NBCO systems are shown in Figs. 3 and 4, respectively. Inspection of these two figures clearly shows that in addition to the Debye component, the Einstein and Schottky contributions are necessary to account for the experimental specific heat. The values of Einstein temperature and N_E are 140 K and 0.7, and 105 K and 0.72 for z=0 and 0.02, respectively. All the contributions to the specific heat are also shown in the same figures which show that the three components considered in the present analysis together give a fairly good representation of our experimental data below 50 K.

V. DISCUSSION

Inspection of Fig. 6 shows interesting variations of the CF parameters both with z and x variations for NBCO and NCCO compounds, respectively. The CF parameters for the $Pr_{2-x}Ce_xCuO_{4-y}$ (PCCO) system⁴² (x=0, 0.05 and 0.15) have also been included in the same figure for comparison. A comparison of the CFP's of the NBCO system to those of the PCCO and NCCO systems shows that the variations in B_2^0 , B_4^0 , and B_6^0 increases with doping at the copper site which is contradictory to doping at the rare-earth site in the *n*-type system. In this context it may be mentioned that, although not appreciable changes are observed in the lattice parameters of the

TABLE III. CF eigenvalues (E) and eigenfunctions for Nd_{1.85}Ce_{0.15}CuO_{4-y} appropriate to ${}^{4}I_{9/2}$.

$E ({\rm cm}^{-1})$	Eigenfunctions
0	0.6520 9/2,±7/2>+0.6280 9/2,±1/2>+0.4146 9/2,±9/2>
102.44	0.8973 9/2,±5/2 > -0.4300 9/2,±3/2 >
163.74	$\pm 0.720 9/2, \pm 7/2 \pm 0.3847 9/2, \pm 1/2 \pm 0.5434 9/2, \pm 9/2 $
214.56	$0.8835 9/2,\pm 3/2\rangle + 0.4349 9/2,\pm 5/2\rangle$
753.36	0.7068 9/2,±9/2 > -0.6691 9/2,±1/2 > +0.1965 9/2,±7/2 >



FIG. 5. Plot of CF levels for different concentrations of z and x in NdBa₂Cu_{3-z}Zn_zO_{7- δ} and Nd_{2-x}Ce_xCuO_{4-y}, respectively. Reported INS energy-level scheme for z=0 (Ref. 21) and x=0.15 (Ref. 7) are included.

NBCO compounds under study yet, the CFP show significant variations. It could be therefore inferred that even small doping in the case of NBCO at the copper site affects both the CFP as well as the superconducting transition temperature, however this effect is not so pronounced in both the PCCO and NCCO systems. Also all the CF parameter values of NCCO are found to be higher than that of PCCO. In the case of NCCO, B_2^0 and B_4^0 have a similar behavior showing a maximum at x=0.16whereas B_6^0 increases monotonically. These parameters do not vary much in the PCCO system. It appears that the changes in B_2^0 and B_4^0 for x=0.16 in NCCO are correlated with superconducting behavior, while the other parameter viz., B_6^0 is relatively insensitive to the changes in cerium concentration. Also B_{2}^{0} , B_{4}^{0} , and B_{6}^{0} are found not to vary in the nonsuperconducting compound.

In conclusion, it may be mentioned that in the present work it has been possible to get a set of crystal-field parameters for both n- and p-type superconductors. These best fitted parameters not only account fairly well for the



FIG. 6. Plot of CFP vs concentration, z in $NdBa_2Cu_{3-z}Zn_zO_{7-\delta}$ and x in $Nd_{2-x}Ce_xCuO_{4-y}$. CFP due to $Pr_{2-x}Ce_xCuO_{4-y}$ are also included for comparison.

magnetic susceptibility data and the specific heat results obtained by us but also agree with the corresponding INS spectra reported by various groups fairly well. It has been possible from this study to make a systematic presentation of the variations in the CF parameters with doping at the rare-earth and copper sites. The specific heat measured by us has also been accounted for by considering different contributions present in these systems. Magnetic anisotropy measurements on single crystals of these compounds using a torque magnetometer are expected to give more conclusive results.

ACKNOWLEDGMENTS

This work was supported by NSTB-DST, New Delhi. We would like to thank Dr. C. K. Subramaniam and Vijayashree Radhakrishnan for providing SQUID data and the Materials Science Research Centre, IIT, Madras for extending cooperation in sample preparation. Thanks are due to Dr. M. V. Sathyanarayana and Dr. S. Rajeswari for the software to calculate the Clebsch-Gordon coefficients. N.R. acknowledges NSTB-DST, New Delhi for financial support.

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