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Superconductivity and Magnetism in Niobium Doped $YBa_2Cu_3O_7$ Related High T_C Ceramics

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ABSTRACT

Magnetic characterization has been performed on the members of the cuprate-niobate $RBa_2Cu_2NbO_8$ (R = Pr, Nd, and La) series and $R_{1.5}Ce_{0.5}Sr_2Cu_2NbO_{10}$ (R = Pr, Eu, Nd, and Sm) series. The PrBCNO samples show a signature in the magnetization of a magnetic ordering at 12 K. The PrCSCNO sample is non-superconducting and shows two distinct orderings at 17K and 53 K. No such magnetic phase transition is observed down to 2 K in the Nd and La based RBCNO materials or the Nd, Sm, and Eu based RCSCNO materials. Measurements of the lower critical field curve, dc irreversibility line, and critical current densities are reported for each of the superconducting NdCSCNO, SmCSCNO, and EuCSCNO compounds.

INTRODUCTION

It is well established that a variety of high temperature superconducting layered cuprate $RBa_2Cu_3O_7$ (R is a rare earth element except Ce, Pr, and Tb) compounds can be readily synthesized with T_C near 90 K. The rare earth elements Ce and Tb do not form the RBCO phase using standard solid-state reaction techniques and Pr forms an isostructural insulating analog.[1] It is widely accepted that the electronic characteristics of the CuO_2 planes in these cuprate structures, specifically the dominant Cu 3d to O 2p energy band hybridization effects, are essential for high-T_c superconductivity to occur, with the CuO chains acting as reservoirs providing the crucial excess charge carriers. Recent efforts aimed at developing better electrical insulators to serve as lattice matched buffer layers in RBCO multi-layer device structures[2] and low dielectric substrates in microwave stripline applications[3] have studied the effects of Niobium doping into the RBCO structural matrix. Initial work[4-7] has demonstrated that $RBa_2Cu_2NbO_8$ (R = La, Pr, and Nd) insulating compounds can be formed using conventional solid-state reaction methods. Rietveld analysis of powder x-ray diffraction as well as neutron diffraction[8,9] have determined the RBCNO structure to be a tetragonal YBCO like structure with the CuO chains fully replaced by NbO_2 planes while leaving the CuO_2 planes intact. In fact, preliminary studies of the electrical transport properties done on these materials show that these RBCNO phases exhibit 3 to 5 orders of magnitude improvement over the parent RBCO compounds in terms of bulk electrical resistivity.[2] Previous transport measurements on the PrBCO system have found the PrBCO phase to be a relatively "weak" electrical insulator due to the effects of variable range hopping of conduction electrons along the CuO chains.[10] Determination of the lattice parameters for these RBCNO phases have demonstrated that the lattice mismatch between the parent RBCO phase to be < 2% along both in-plane and out-of-plane directions making these materials suitable choices for epitaxially grown RBCO/RBCNO multi-layer thin films.[11] The RBCNO crystallographic structure is shown in figure 1. Additional interest in these cuprate-niobate systems has also been recently sparked by the suggestion that some of these materials might become superconducting if they could be properly doped based on the similarity of their electronic band structure to that of YBCO.[12] The parent YBCO system exhibits band features near the Fermi energy, namely a pair of half-filled, nearly degenerate antibonding σ^* subbands. To date such attempts to raise the Cu oxidation state in the CuO_2 planes by doping holes into these RBCNO materials through chemical substitution such as Ca^{2+} and Sr^{2+} in for La^{3+} and Ti^{4+} in for Nb^{5+} have been unsuccessful.[8]

Li et al[13,14] was the first to investigate the cuprate-niobate $Nd_{1.5}Ce_{0.5}Sr_2Cu_2MO_{10}$ (M = Nb or Ta) insulating compound. Cava et al[15] later refined the preparation technique and was successfully able to make $Nd_{1.5}Ce_{0.5}Sr_2Cu_2NbO_{10}$ (NdCSCNO) superconducting with a T_C of approximately 28 K. Recently, Goodwin et al[16] was successfully able to form two additional isostructural superconducting phases $R_{1.5}Ce_{0.5}Sr_2Cu_2NbO_{10}$ (R = Eu and Sm) with T_C for these materials around 28 K. Structural analysis of these new RCSCNO phases from powder x-ray diffraction data have shown that in addition to the local substitution of NbO_2 planes for the CuO chains in the RBCO structure, a fluorite structured $(R_{1.5}Ce_{0.5})O_2$ layer fully replaces the rare earth layer with strontium replacing barium. In addition these studies have shown that the length of the unit cell in the c-direction is doubled due to a glide plane introduced by the R_2O_2 fluorite structure. Half of the RCSCNO crystallographic structure is shown in figure 1.

In this paper we present results on the magnetic properties of the $RBa_2Cu_2NbO_8$ (R = Pr, La, and Nd) compounds and the superconducting and magnetic properties of the $R_{1.5}Ce_{0.5}Sr_2Cu_2NbO_{10}$ (R = Pr, Nd, Sm, and Eu) compounds. The discussion covers the issue of the correlation between the absence of superconductivity observed in the Pr based phases and the appearance of large antiferromagnetic ordering transitions.

DETAILS

The polycrystalline samples of RBCNO were synthesized through conventional solid-state reaction methods. Stoichiometric amounts of high-purity (99.99% or better) Pr_6O_{11}, $BaCO_3$, CuO, Nb_2O_5, La_2O_3, and Nd_2O_3 dried powders were appropriately mixed, ground, and reacted in air at 1000°C for 12 hours. Each calcined mixture was then reground and the firing process repeated. Subsequently, the powders were pressed into pellets, sintered in air at 1025°C for an additional 24 hours, and then allowed to furnace cool back down to room temperature.

The Polycrystalline samples of RCSCNO were prepared using stoichiometric amounts of high purity (99.99% or better) CeO_2, Nd_2O_3 , Pr_6O_{11} , Sm_2O_3 , Eu_2O_3 , $SrCO_3$, CuO, and Nb_2O_5 powders that were appropriately weighed, ground together, and pressed into 3/8 inch pellets. The finished pellets were placed in alumina crucibles and sintered at 1120 °C for 80 hours in a slightly pressurized (approximately 30 kPa) oxygen atmosphere and then allowed to furnace cool to room temperature. Samples were then reground, pressed into pellets, and the firing process repeated.

The magnetization data taken on the sintered RBCNO and RCSCNO test samples were obtained using a commercially available Quantum Design SQUID magnetometer.

RESULTS

The magnetic susceptibilities of the Pr, Nd, and La based RBCNO samples were examined up to 300 K in a field of 5000 Oe. The results are shown in Fig. 2 with the magnetic susceptibilities plotted as a function of temperature. A previous study[5] found that the effective magnetic moments of the rare earth ions in the PrBCNO, NdBCNO, and LaBCNO compounds, determined using Curie-Weiss fits to the data, were 2.81, 2.07, and 0.3 μ_B respectively. The differences in these values from the corresponding free ion values were attributed to the effects of crystalline fields in these compounds.

Moreover, the PrBCNO system shows a distinct signature of a magnetic transition occurring ~ 12 K while there is no evidence of such magnetic ordering in the NdBCNO or LaBCNO systems down to 1.85 K. Recent neutron scattering data has indicated that the NdBCNO material orders down at 1.7 K.[9]

Zero-field cooled magnetization data for the Pr, Nd, Sm, and Eu based RCSCNO samples were obtained up to 30 K in a field of 10 Oe. The results are shown in figure 3 with the magnetization data plotted as a function of temperature. The NdCSCNO, SmCSCNO, and EuCSCNO samples all showed evidence of a superconducting transition occurring below 28 K. The broad superconducting transitions seen in figure 3 were attributed to inhomogeneity in the doping of Ce atoms within these compounds. Recent studies have shown that Ce doping is the mechanism for providing excess hole charge carriers onto the CuO_2 planes.[16] No superconductivity has been observed to occur in the PrCSCNO material.

The lower critical field H_{C1} profiles for the Nd, Sm, and Eu based superconducting RCSCNO phases are shown in figure 4 with the data plotted as a function of temperature. The field of first vortex entry was chosen to be the field where the magnetization versus field data, at a given temperature, began to reasonably deviate from linearity (< .999 in goodness-of-fit values). The onset of this deviation providing a measure of the extent of the diamagnetic response, i.e. magnetic flux expulsion, within these high T_C superconductors. The temperature behavior of the H_{C1} lines for these compounds do not show any indication of saturation at low temperatures as might be expected for intrinsic BCS type behavior.[17] Similar behavior in the temperature dependence of H_{C1} has been previously observed in magnetization studies on oriented polycrystals of RBCO.[18]

The dc irreversibility phase lines for NdCSCNO, SmCSCNO, and EuCSCNO test specimens are shown in figure 5. The data points comprising the irreversibility phase curves in the thermodynamic H-T plane were obtained by determining the point of departure in temperature of the Meissner signal (field cooled measurements) from the shielding signal (zero-field cooled measurements) as a function of the applied magnetic field. Above and to the right of these lines, the samples have reversible magnetic behavior, while below and to the left of these lines, the sample demonstrates irreversible behavior due to flux pinning effects within these materials. A recent investigation[19] of the supercondcuting members of the RCSCNO family of compounds suggests that the phase boundary between the reversible and irreversible behavior in these RCSCNO materials may closely coincide with the critical phase line $T_C(H)$.

The critical current densities $J_C(H,T)$ for NdCSCNO, SmCSCNO, and EuCSCNO are shown in figure 6 as a function of field at 6 K. In lieu of direct electrical transport measurements, the estimates for these critical currents were deduced from high field hysteresis data using the Bean's critical state model. According to the Bean model J_C [A/cm^2] is given by the relationship,[20] $J_C = 15 * \Delta M/R$, where ΔM [emu/cm^3] is the width of the hysteresis loop and R [cm] is the average radius of the superconducting grains. The zero-field critical current densities, $J_C(0,6K)$, for the Eu, Sm, and Nd based RCSCNO systems were determined from figure 6 to be ~ 4.7 x10^4 , 3.3x10^4 , and 2.7x10^4 A/cm^2 respectively. These numbers are similar to those reported for sintered $Tl_2Ba_2Ca_2Cu_3O_{10}$[21] within one order of magnitude of those originally reported for sintered $Bi_4Sr_3Ca_3Cu_4O_{16}$[22] and two orders of magnitude smaller than sintered $YBa_2Cu_3O_7$.[23] However it should be noted that for most polycrystalline high T_C materials the Bean critical state model really only provides a rough estimate of the intragrain critical current density, $J_C(H,T)$, because the magnetic-field dependence is neglected and hence the magnetization at which the flux penetrates to the center of a sample depends only on the temperature.

The magnetic susceptibilities of the Pr, Nd, Sm, and Eu based RCSCNO samples were examined from 30 to 300 K. The results are shown in figure 7 with the suceptibilities plotted as a function of temperature. The suceptibilities for the Nd, Sm, and Eu analogs were generated in a 1000 Oe field. The suceptibility for the Pr analog was generated in both a 500 Oe and a 5000 Oe field. The magnetic susceptibility of the Nd and Sm based RCSCNO systems both showed a Curie-Weiss type dependence above 30 K. On the other hand, no such Curie-Weiss behavior was observed to occur in EuCSCNO. The result for EuCSCNO was consistent with the Eu ion being in the +3 valence state since the theoretical value of the effective moment for the Eu^{+3} ion calculated from Hund's rules is zero. A key feature in the susceptibility data for the PrCSCNO compound is the two distinct ordering transitions that are observed to occur at 17 K and 53 K. The strength of the transitions were observed to be strongly field dependent. It is believed, based on the nature of the magnetic transitions observed in PrBCO and PrBCNO, that the first magnetic phase ordering is due to the Pr ions and that the second ordering transition may be due to the Cu magnetic sublattice. The ordering temperature of the Cu in the PrBCO structure has been observed to be strongly effected by the removal of oxygens from the CuO chains.[1] No such transitions were observed to occur in the other members of the RCSCNO series down to 2 K. The effective magnetic moments of the rare earth ions in the PrCSCNO, NdCSCNO, and SmCSCNO compounds have been previously reported[16] to be 2.6, 2.97, and 0.42 μ_B respectively. Again the values of these moments are interpreted as being reduced from the corresponding free ion values due to crystalline field effects.

Discussion

One of the more anamolous features seen in the magnetic suceptibility data for the cuprate-niobate PrBCNO and PrCSCNO insulating compounds are the rather high T_N values for the antiferromagnetic (AFM) ordering transitions. Similar studies on PrBCO have demonstrated that an AFM ordering on the Pr sublattice occurs at $T_N = 17$ K.[24,25] This AFM ordering temperature is a factor of 10 higher than expected, based on RKKY scaling of T_N from the other RBCO compounds, where the next highest T_N occurs for GdBCO with T_N = 2.2 K. Still in other related experiments Soderholm et al.[26] have shown the CmBCO analog to be nonsuperconducting and to exhibit a magnetic ordering as well at an anomalously high temperature of 22 K. In contrast, superconductivity has been directly observed in compounds where the T_N is consistent with the other rare earth members, such as $Pr_{2-x}Ce_xCuO_4$.[27] A recent study[28] suggests that a correlation may exist between the appearance of unusually high magnetic ordering temperatures and the absence of superconductivity due to hybridization effects. In some cases, the hybridization effects within these compounds are believed to affect superconductivity, either through mediation of magnetic interactions which lead to pair breaking and/or by leading to hole localization.[1] This belief is based on the fact that in the absence of conduction electrons to mediate the RKKY interaction, some form of hybridization of the extended 4f orbitals with the d and p electrons from the nearby Cu and O atoms is required to mediate a superexchange interaction between the Pr ions. This point is further strengthened by neutron diffraction results that show that in oxygen-deficient $PrBCO_6$, the magnetic ordering temperature for the Pr sublattice decreases from 17 K to below 10 K with an accompanying decrease in dimensionality of the ordering from 3D to 2D.[29,30] Recent neutron diffraction studies on the PrBCNO system show the dimensionality of the magnetic ordering to be quasi-2D consistent with a smaller value of T_N =12 K.[9] This type of evidence for hybridization has not been observed in the other RBCO materials or $Pr_{2-x}Ce_xCuO_4$, which show superconductivity and have magnetic ordering temperatures below 2.2 K, presumably mediated by dipolar interactions.

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FIGURE CAPTIONS

1) Crystallographic structures of (b) RBCNO and (c) RCSCNO compounds. The figure for RCSCNO shows only one half of a unit cell. The structure for (a) the parent RBCO compounds is also provided for comparison.

2) The magnetic susceptibilities of the Pr, Nd, and La based RBCNO samples plotted as a function of temperature up to 300 K in a field of 5000 Oe. PrBCNO shows an AFM ordering ~ 12 K. No such magnetic transition was observed down to 1.85 K in the other RBCNO members.

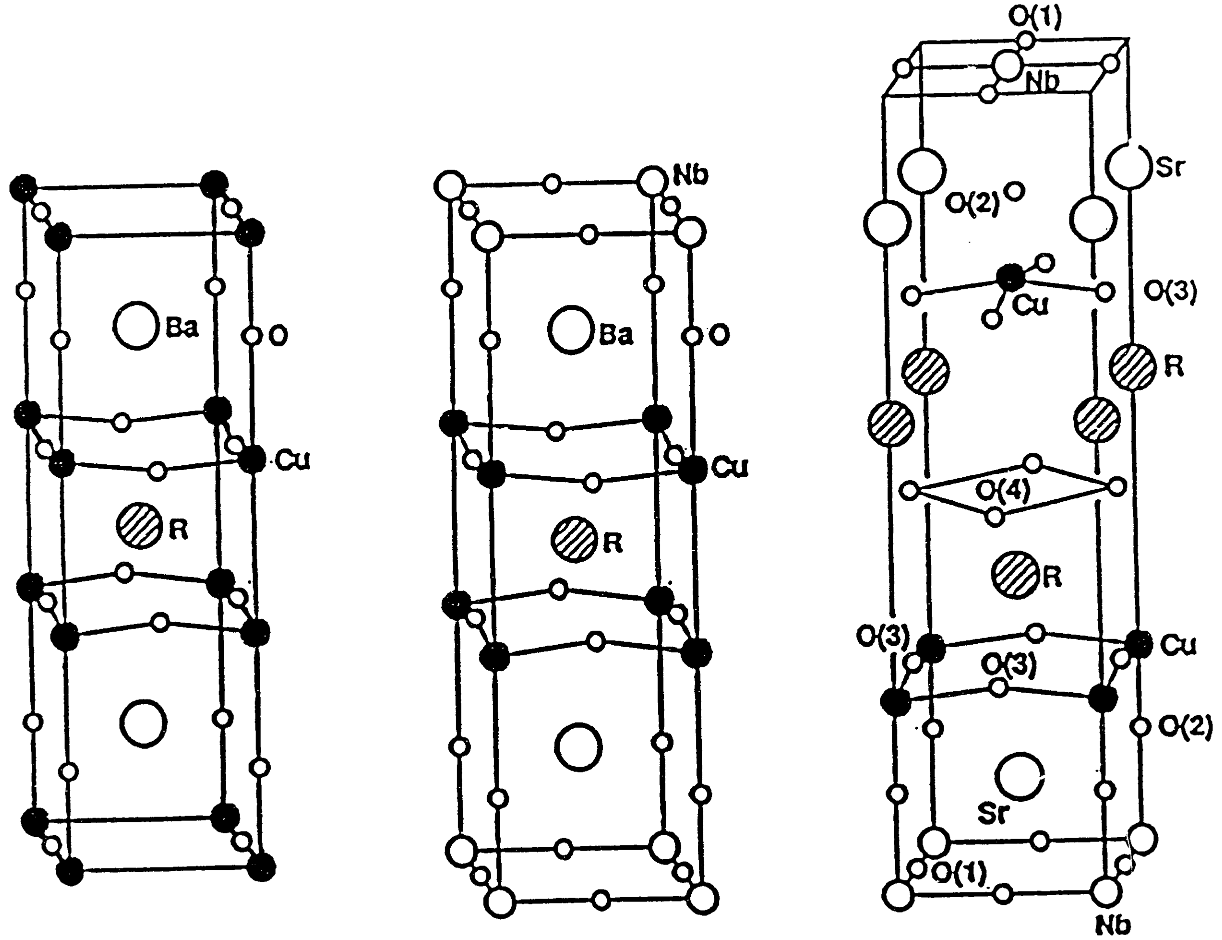
3) $4\pi M$ data for the RCSCNO compounds plotted as a function of temperature in an applied field of 10 Oe. A broad superconducting transition occurs for the Nd, Eu, and Sm analogs. No superconductivity occurs in the PrCSCNO phase.

4) The H_{C1} lines plotted as a function of temperature for all three superconducting RCSCNO phases. The error bars in obtaining the values of H_{C1} in these materials is estimated to be ± 1 G.

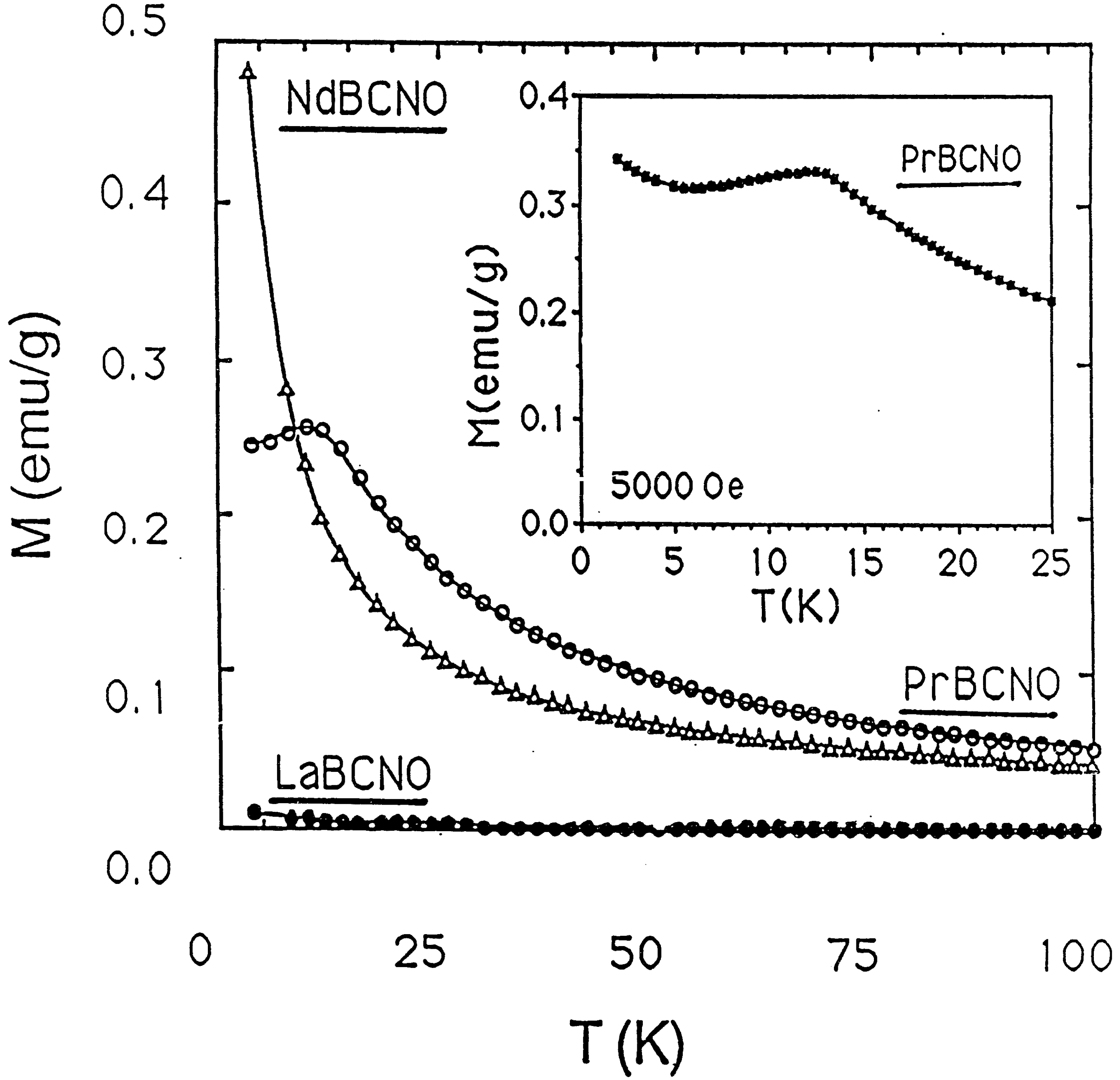
5) The H-T Irreversibility phase lines for the Nd, Sm, and Eu based RCSCNO materials. The lines shown in this figures are quasi-de Almeida-Thouless curve fits to the data. The error in the values of $T_{irreversibility}$ are estimated to be ± .5 K

6) Critical current density profiles deduced from the Bean critical state model for the superconducting RCSCNO analogs plotted as a function of magnetic field.

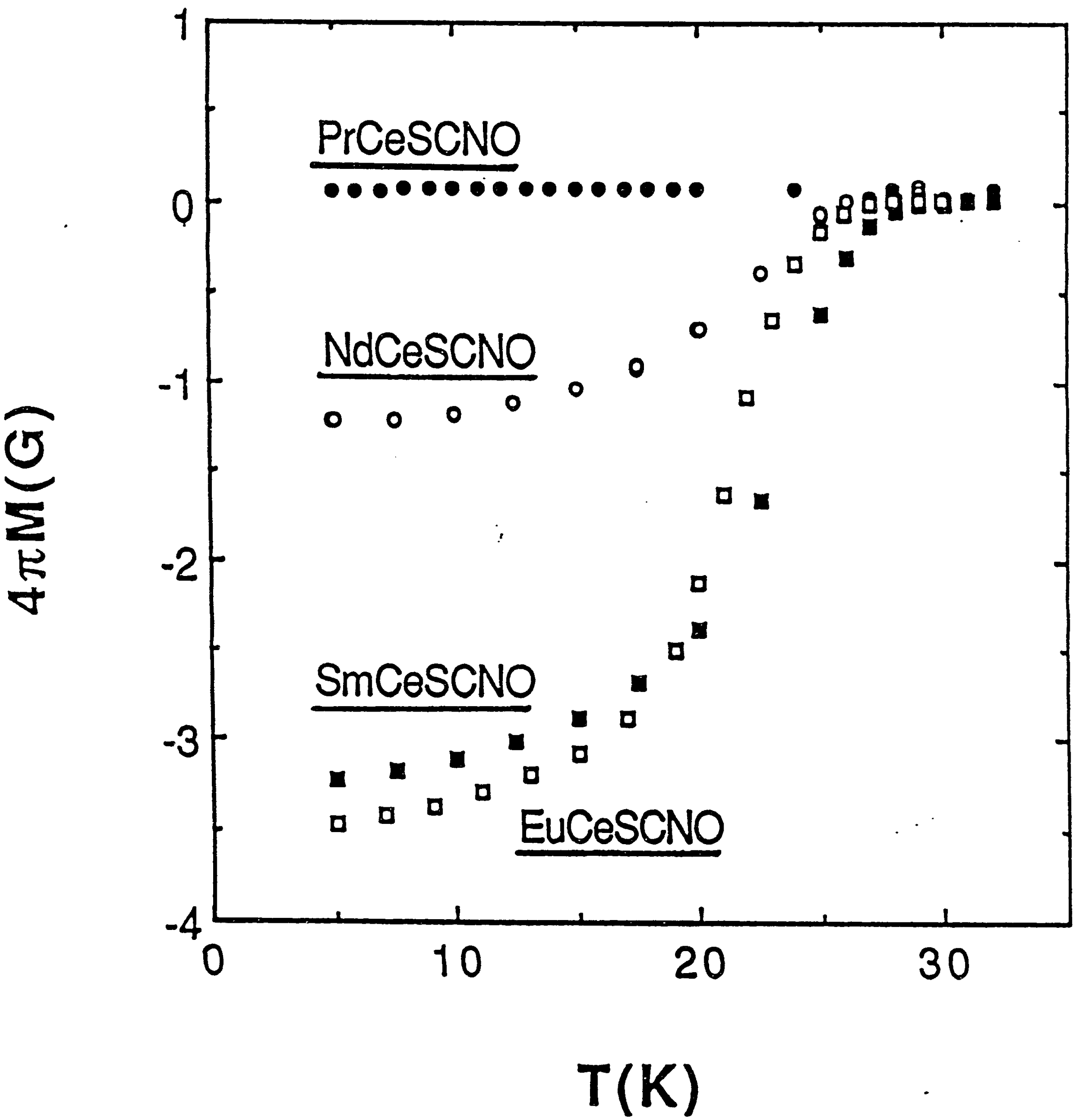
7) The magnetic susceptibilities of the Pr, Nd, Sm, and Eu based RCSCNO samples plotted as a function of temperature. The suceptibility for NdCSCNO has been reduced by a factor of 5 and that of EuCSCNO by a factor of 2 for clarity. The PrCSCNO phase shows two distinct magnetic phase transitions at 17 K and 53 K that are strongly field dependent. No such transitions are observed to occur in the other three RCSCNO members.

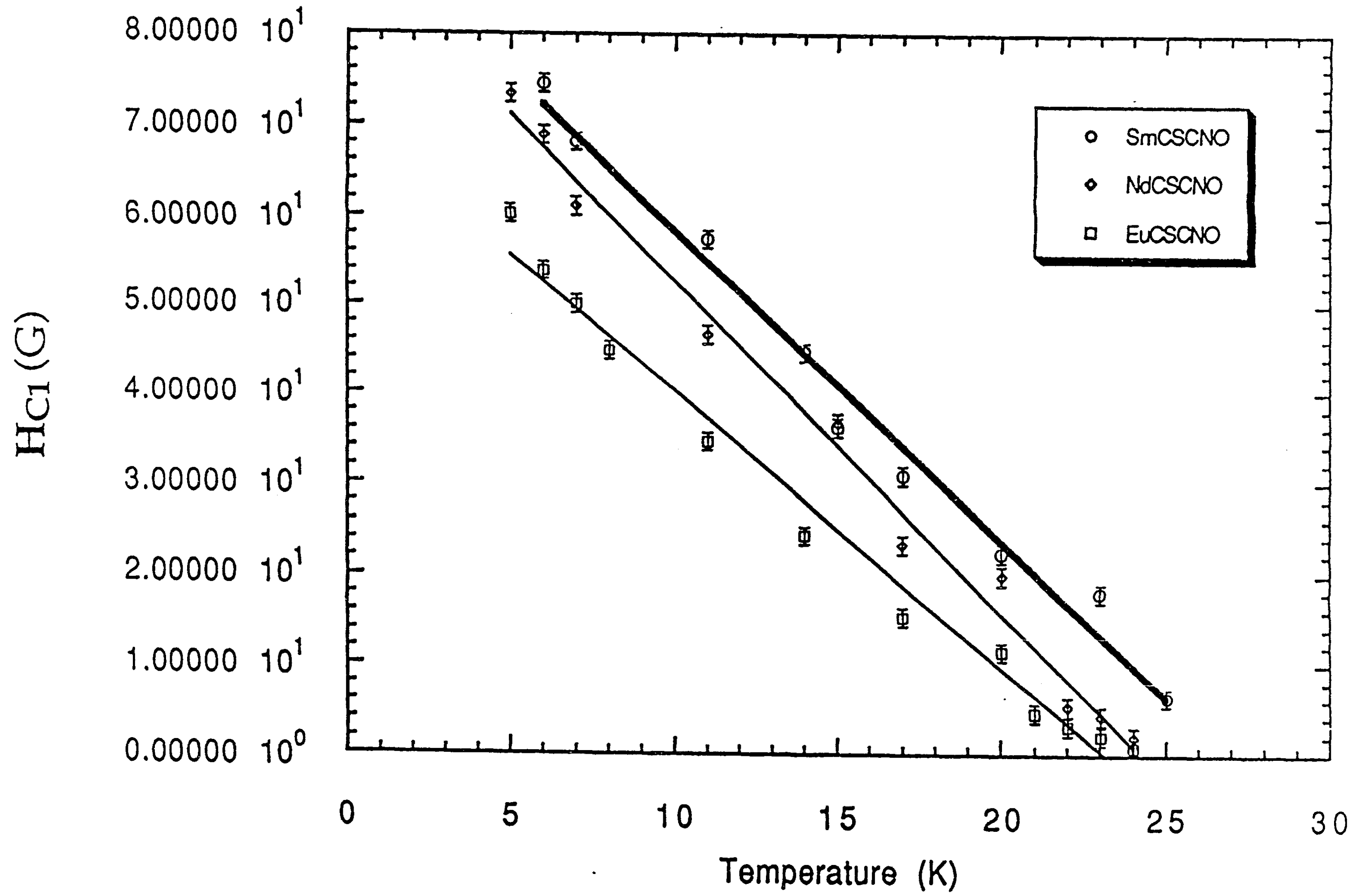


(a) (b) (c)

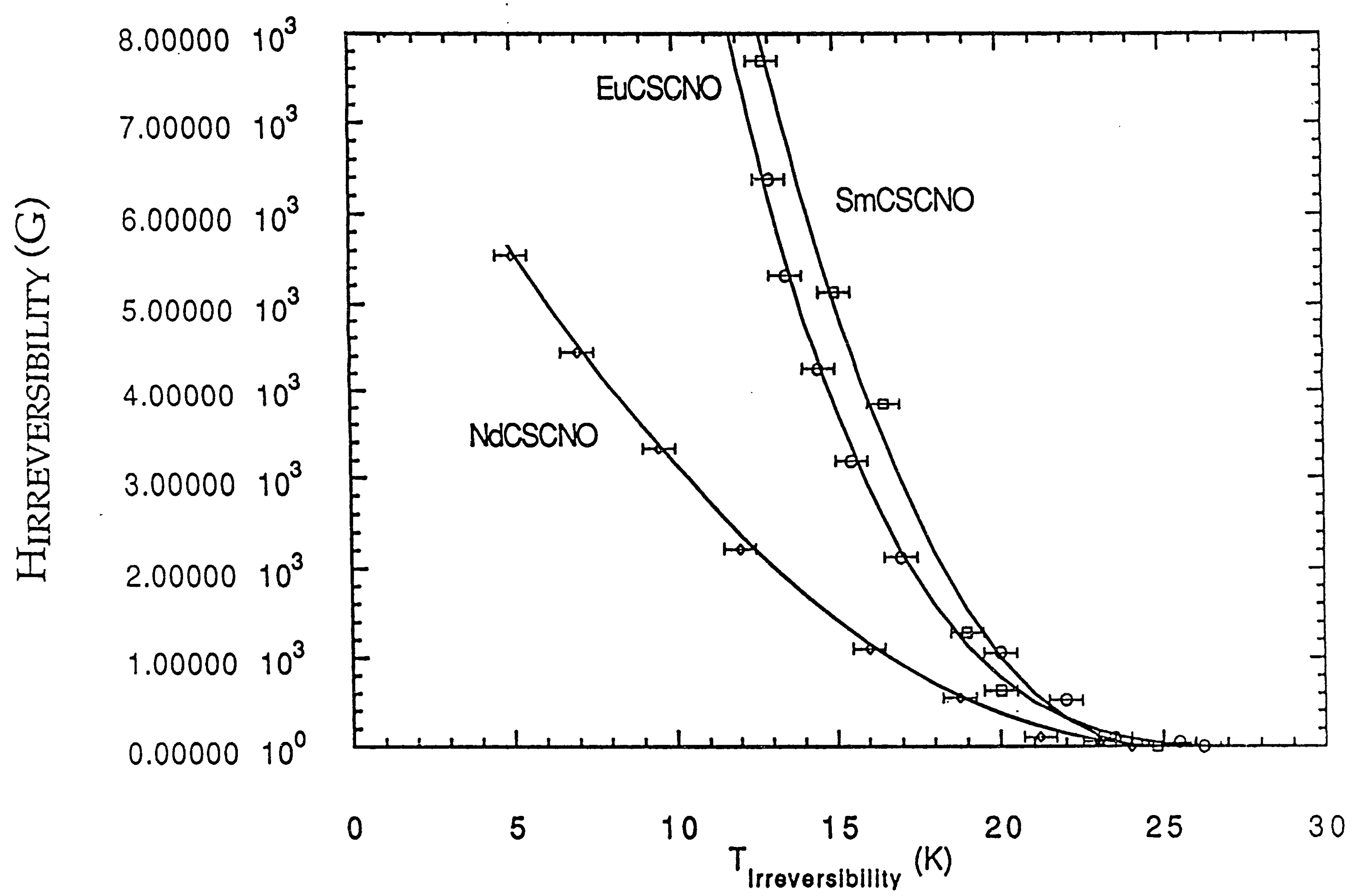


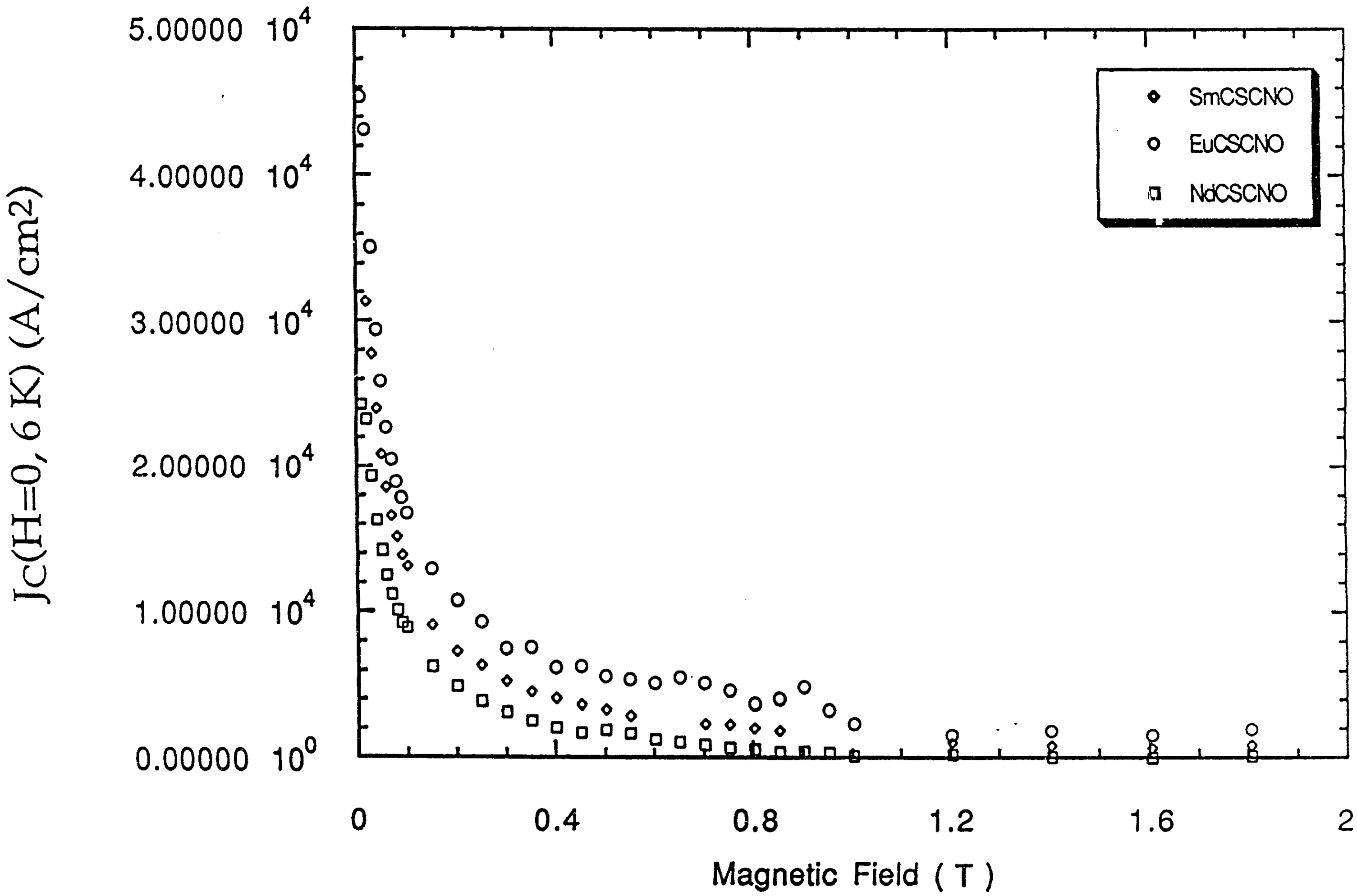
NdBCNO
PrBCNO
LaBCNO
M (emu/g)
T (K)
0.0
0.1
0.2
0.3
0.4
0.5
0
25
50
75
100
PrBCNO
5000 Oe
M(emu/g)
T(K)


PrCeSCNO
NdCeSCNO
SmCeSCNO
EuCeSCNO
1
0
-1
-2
-3
-4
0
10
20
30
4πM(G)
T(K)

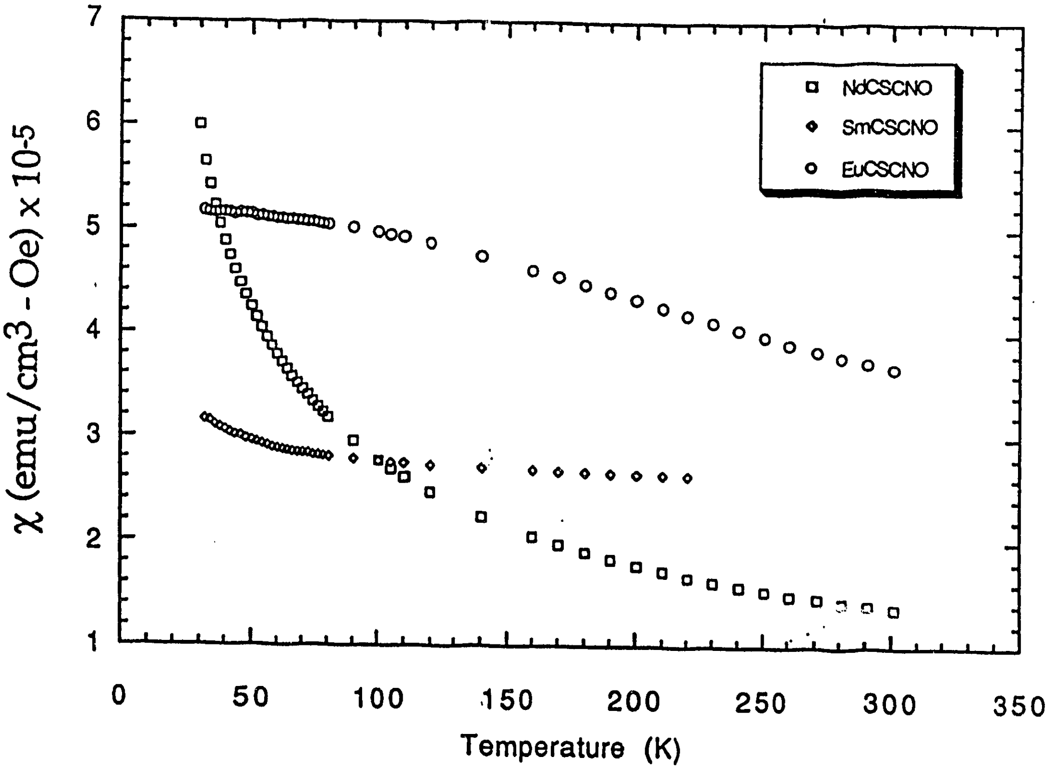


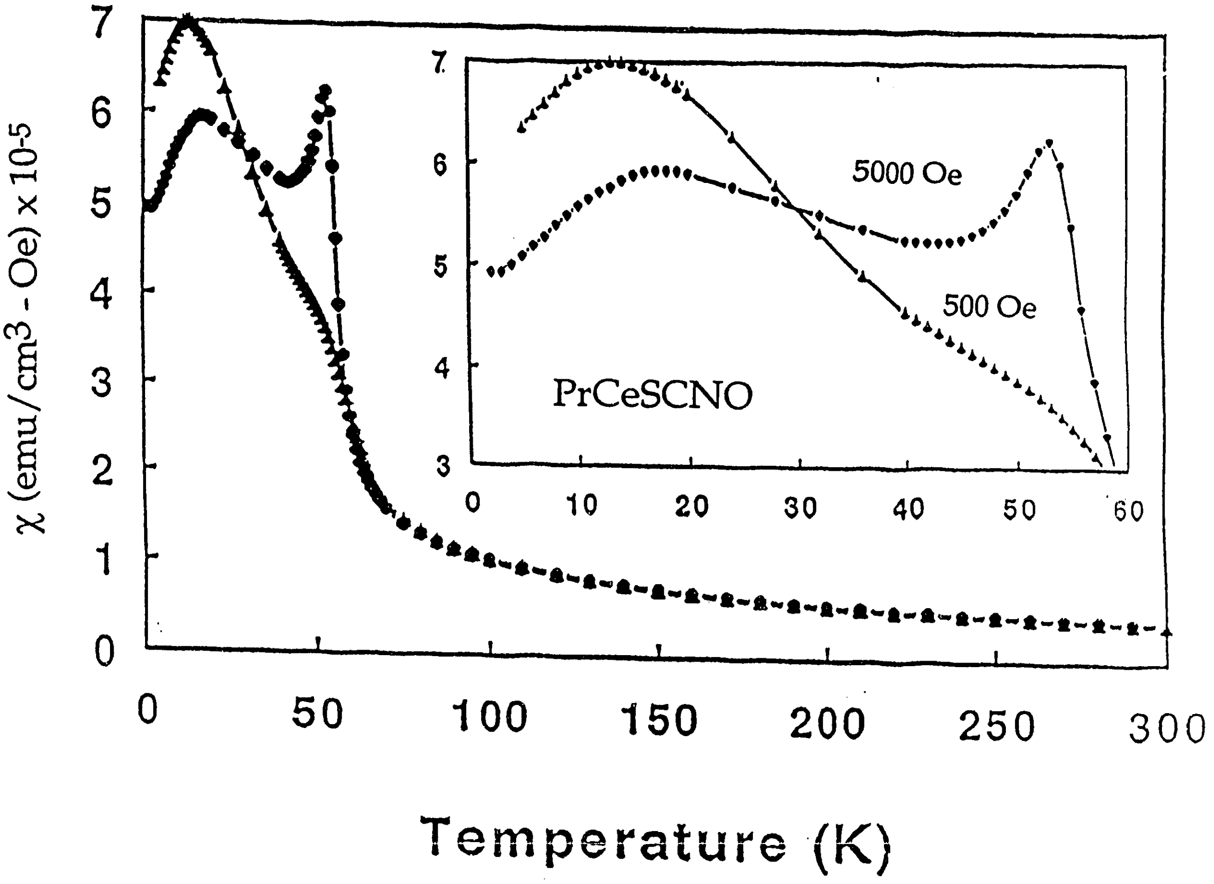
SmCSCNO
NdCSCNO
EuCSCNO
8.00000 10^1
7.00000 10^1
6.00000 10^1
5.00000 10^1
4.00000 10^1
3.00000 10^1
2.00000 10^1
1.00000 10^1
0.00000 10^0
0
5
10
15
20
25
30
Temperature (K)
Hc1 (G)


EuCSCNO
SmCSCNO
NdCSCNO
8.00000 10^3
7.00000 10^3
6.00000 10^3
5.00000 10^3
4.00000 10^3
3.00000 10^3
2.00000 10^3
1.00000 10^3
0.00000 10^0
0
5
10
15
20
25
30
HIRREVERSIBILITY (G)
TIrreversibility (K)



Jc(H=0, 6 K) (A/cm2)
5.00000 10^4
4.00000 10^4
3.00000 10^4
2.00000 10^4
1.00000 10^4
0.00000 10^0
0
0.4
0.8
1.2
1.6
2
Magnetic Field (T)
SmCSCNO
EuCSCNO
NdCSCNO


NdCSCNO
SmCSCNO
EuCSCNO
χ (emu/cm3 - Oe) x 10-5
Temperature (K)


5000 Oe
500 Oe
PrCeSCNO
χ (emu/cm3 - Oe) x 10-5
Temperature (K)

END

DATE
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