

ANISOTROPIC PARAMAGNETIC SUSCEPTIBILITY OF $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ DUE TO THE CRYSTALLINE ELECTRIC FIELD: POINT CHARGE CALCULATIONS*

H. S. LESSURE, E. B. BOLTICH, S. G. SANKAR, W. E. WALLACE and D. E. LAUGHLIN

MEMS Dept. and Mellon Institute, Carnegie Mellon University, Pittsburgh, PA, 15213 (U.S.A.)

(Received June 15, 1988)

Summary

Magnetic susceptibility measurements of $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ (where $\text{R} \equiv$ rare earth ion) indicate that these compounds are paramagnetic above T_c . When $\text{R} \equiv \text{Dy}$, Er or Nd , there appears to be a considerable degree of anisotropy in the magnetic susceptibility between the c axis and the a - b plane. This property may help align these compounds in external magnetic fields. The nature and extent of this anisotropy is of major theoretical interest. In this paper, we report on calculations of the magnetic susceptibility in the paramagnetic regime of the $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ (where $\text{R} \equiv \text{Dy}$, Er and Nd and $0 < x < 1$). The point charge model was employed utilizing the Stevens operator equivalents. The calculations show that the crystalline field acting on the 4f electrons of the rare earth ions plays a reasonable role in modifying the susceptibility to temperatures up to 300 K. The susceptibility was also found to be anisotropic. The crystal field coefficients evaluated from the point charge model appear to be consistent with experimental results for $\text{R} \equiv \text{Dy}$, Er and Nd and for oxygen stoichiometry between 6 and 7.

1. Introduction

Magnetic susceptibility measurements of $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ compounds (where $\text{R} \equiv$ rare earth) indicate that they are paramagnetic above the superconducting transition temperature T_c [1]. Measurements reveal a considerable degree of anisotropy in the magnetic susceptibility between the c axis and the a - b plane in aligned powder samples or aligned sintered samples [2-5]. The nature and extent of this anisotropy is of major theoretical interest. In this paper, we report our recent work on the calculation of the

*Paper presented at the 18th Rare Earth Research Conference, Lake Geneva, WI, September 12 - 16, 1988.

magnetic susceptibility in the paramagnetic regime for $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$ (where $\text{R} \equiv \text{Nd, Dy and Er}$ and $x = 0$ or 1). The crystal field parameters (B_n^m 's) were calculated on the basis of the point charge model. The present calculations indicate that the crystalline electric field acting on the $4f$ electrons of the rare earth ions produces a significant anisotropy in the susceptibility and plays a reasonable role in modifying the susceptibility to temperatures up to and exceeding 300 K.

The point charge model, despite its questionable validity, has successfully shown that the second order crystal field terms predict maximal susceptibility along the c axis for high T_c superconductors with rare earth ions having negative second-order Stevens factors, such as neodymium and dysprosium. The situation is analogous to that found for the $\text{Nd}_2\text{Fe}_{14}\text{B}$ -based permanent magnets [6, 7]. For ions having positive second-order Stevens factors, e.g. erbium, the situation is reversed, the anisotropy favoring a planar moment. Thus, relatively simple point charge calculations can give an indication of the experimental anisotropies likely to be observed in the R-Ba-Cu-O superconductors which give the materials an Ising-like or XY-like character.

2. Calculations

The calculations were performed using a modified version of a computer program described in an earlier publication [8]. The free-ion wavefunctions are perturbed by both the crystal field and the applied magnetic field [9]. The matrix elements of the magnetic hamiltonian are added to those of the crystal field to form the complete hamiltonian, which is then diagonalized by standard methods, to obtain the eigenvalues and eigenvectors. Once the eigenvalues and eigenvectors are determined, the free energy and magnetic moment are calculated. The components of these moments are obtained from the expectation values of J_z , J_+ and J_- . The expectation values of J_z , J_+ and J_- in turn, are calculated from the components of the corresponding eigenvector. The magnetic moment follows directly.

3. Results and discussion

Both tetragonal and orthorhombic modifications of the 1-2-3 superconductors were considered. The structural parameters were obtained from neutron diffraction values for $\text{YBa}_2\text{Cu}_3\text{O}_6$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$ [10 - 12]. Charge assignments were taken as R^{3+} , Ba^{2+} , O^{2-} , and $\text{Cu}^{5/3+}$ and $\text{Cu}^{7/3+}$ for the tetragonal and orthorhombic cases respectively. Copper sites were thus taken to have averaged values (different copper sites were not distinguished by charge) and oxygen was assigned a valency of -2 as a first approximation.

TABLE 1

Comparison of calculated ground state moments for $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$ ($\text{R} \equiv \text{Nd, Dy and Er}$ for $x = 0$ or 1)

Compound	Ground state moments ($\mu_{\text{B}} \text{ cell}^{-1}$)		
	m_{a}	m_{b}	m_{c}
$\text{ErBa}_2\text{Cu}_3\text{O}_6$	5.5906	5.5906	0.6351
$\text{ErBa}_2\text{Cu}_3\text{O}_7$	3.1270	7.1332	0.4694
$\text{DyBa}_2\text{Cu}_3\text{O}_6$	0.5259	0.5259	8.6645
$\text{DyBa}_2\text{Cu}_3\text{O}_7$	0.0784	0.0537	9.9872
$\text{NdBa}_2\text{Cu}_3\text{O}_6$	1.0038	1.0038	1.3658
$\text{NdBa}_2\text{Cu}_3\text{O}_7$	0.9594	0.6740	2.4792

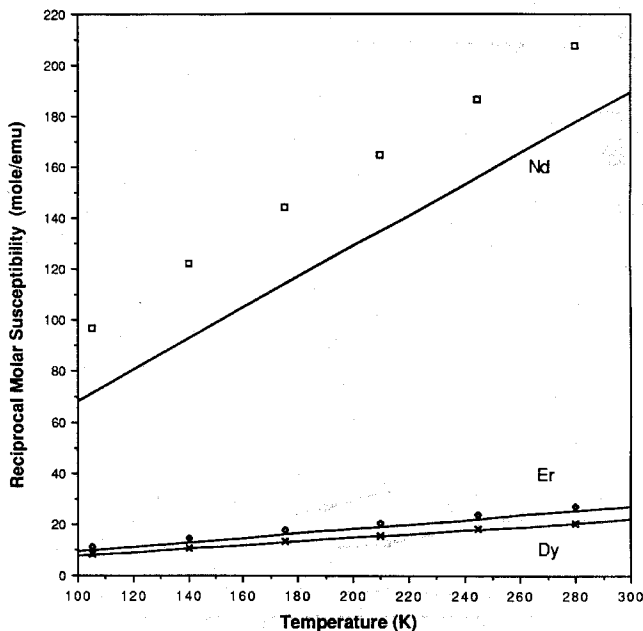


Fig. 1. Calculated reciprocal molar susceptibility (χ^{-1}) (shown in solid lines) with experimental values (symbols) taken from Tarascon *et al.* [1]. Values are indicated for $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$ ($\text{R} \equiv \text{Nd, Dy and Er}$) over the temperature range 100 - 300 K. Curves and data are for $\text{R} \equiv \text{Nd}$ in orthorhombic form and for $\text{R} \equiv \text{Dy and Er}$ in tetragonal form.

The calculated ground state magnetic moments are given in Table 1 for $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_6$ (tetragonal) and $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_7$ (orthorhombic) where $\text{R} \equiv \text{Nd}$, Dy and Er . From Table 1, one finds the preference for neodymium and dysprosium moments to align along the c axis and the preference for erbium moments to lie in the a - b plane at $T = 0$ K. This correlates with low temperature magnetic structure determined by neutron diffraction [13]. The results for $\text{R} \equiv \text{Ce}$, Pr , Nd , Tb , Dy , Ho , Er , Tm , and Yb have been calculated and will appear in an extended version of this work.

Our initial results for susceptibilities are shown in Fig. 1 for $\text{R} \equiv \text{Nd}$, Dy and Er where calculated curves are compared with representative experimental values from the literature [1]. In our calculations, the average molar susceptibility follows a Curie law with Curie constants slightly lower than the free ion values in agreement with the experimental data in the temperature range shown. The absolute values of susceptibility are good to within approximately 10% of the experimental values for $\text{R} \equiv \text{Dy}$ and Er and within

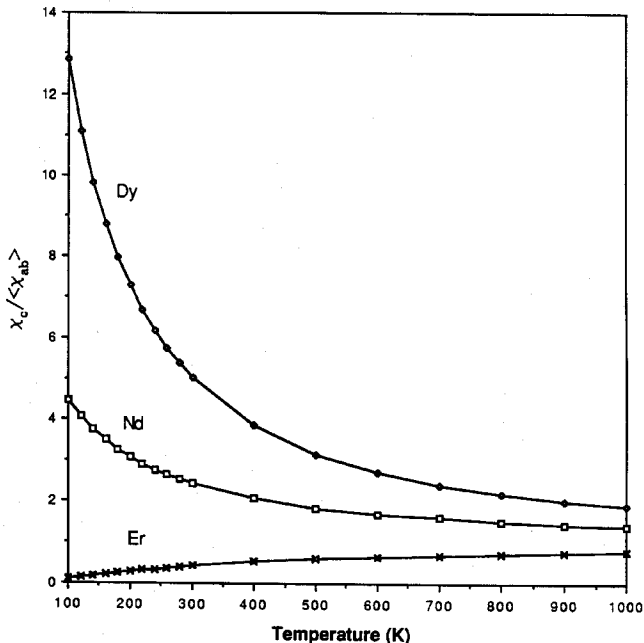


Fig. 2. Calculated axial anisotropy ($\chi_c / \langle \chi_{ab} \rangle$) vs. temperature for orthorhombic structures (lines drawn to guide the eye).

approximately 25% for $R \equiv \text{Nd}$. The relatively large difference between experimental and calculated values of susceptibility in the case $R \equiv \text{Nd}$ may be viewed in two ways: (i) it has recently been shown that the orthorhombic neodymium compound is rather sensitive to stoichiometry [14] and secondary phases could cause the experimental value to be in error or, (ii) the present calculation neglects magnetic interactions between the RE ions.

The calculated anisotropy in susceptibility between the c axis and the a - b plane is shown in Fig. 2 for the orthorhombic case in the temperature range $100 < T < 1000$ K. The a - b plane susceptibility is taken as the average between the a and b directions.

The anisotropy in the a - b plane is shown in Fig. 3 and should be particularly significant for the XY-like systems [15].

Having obtained the energy levels, the partition function, free energy, heat capacity, and entropy of the material were calculated and compared with experiment. The calculated splittings lead to heat capacity and entropy

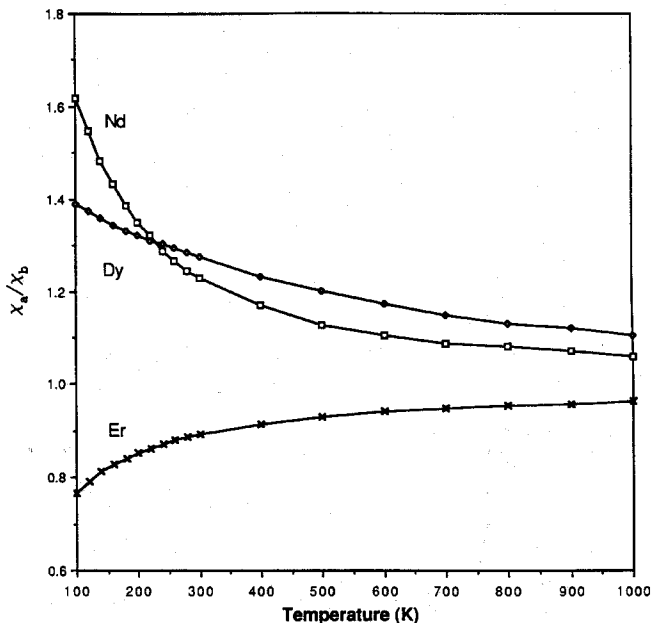


Fig. 3. Calculated in plane anisotropy (χ_a/χ_b) vs. temperature for orthorhombic structures (lines drawn to guide the eye).

curves which agree qualitatively with the experimental Schottky anomaly due to the first excited doublets for R \equiv Nd [16], Dy [17] and Er [14].

Crystal field calculations based on the point charge model for $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$ are capable of describing qualitatively the paramagnetic anisotropies observed in experiment. This may allow even the simple theory to have some predictive value for paramagnetic alignment and could have implications for magnetic ordering.

Acknowledgments

We would like to thank J. D. Livingston, S. Simizu, G. Bellesis, J. Lukin, S. A. Friedberg, S. Fine and M. Greenblatt for their stimulating discussion and communication of results prior to publication. H.S.L. was supported by a graduate fellowship from the MEMS Department, Carnegie Mellon University.

References

- 1 J. M. Tarascon, W. R. McKinnon, L. H. Greene, G. W. Hull and E. M. Vogel, *Phys. Rev. B*, **36** (1987) 226.
- 2 D. E. Farrell, B. S. Chandrasekhar, M. R. DeGuire, M. M. Fang, V. G. Kogan, J. R. Clem and D. K. Finnemore, *Phys. Rev. B*, **36** (1987) 4025.
- 3 R. H. Arendt, A. R. Gaddipati, M. F. Garbauskas, E. L. Hall, H. R. Hart, Jr., K. W. Lay, J. D. Livingston, F. E. Luborsky and L. L. Schilling, in M. B. Brodsky, R. C. Dynes, K. Kitazawa and H. L. Tuller (eds.), *High Temperature Superconductors*, Materials Research Society, Pittsburgh, PA, 1988, p. 203.
- 4 J. D. Livingston, H. R. Hart, Jr. and W. P. Wolf, *J. Appl. Phys.*, **64** (1988) 5806.
- 5 J. D. Livingston and H. R. Hart, Jr., private communication (1988).
- 6 J. M. Cadogan and J. M. D. Coey, *Phys. Rev. B*, **30** (1984) 7326.
- 7 D. Givord, H. S. Li and R. Perrier de la Bathie, *Solid State Commun.*, **51** (1984) 857.
- 8 E. B. Boltich, *J. Appl. Phys.*, **63** (1988) 3124.
- 9 M. T. Hutchings, *Solid State Phys.*, **16** (1966) 227.
- 10 A. Santoro, S. Miraglia, F. Beech, S. A. Sunshine, D. W. Murphy, L. F. Schneemeyer and J. V. Wasczak, *Mater. Res. Bull.*, **22** (1987) 1007.
- 11 J. Y. Henry, P. Bulet, G. Roullet, P. Bacher, M. J. G. M. Jurgens and J. Rossat-Mignod, *Solid State Commun.*, **64** (1987) 1037.
- 12 Y. LePage, T. Siegrist, S. A. Sunshine, L. F. Schneemeyer, D. W. Murphy, S. M. Zahurak, J. V. Wasczak, W. R. McKinnon, J. M. Tarascon, G. W. Hull and L. H. Greene, *Phys. Rev. B*, **36** (1987) 3617.
- 13 J. W. Lynn, W.-H. Li, Q. Li, H. C. Ku, H. D. Yang and R. N. Shelton, *Phys. Rev. B*, **36** (1987) 2374.
- 14 H. Nozaki, S. Takekawa and Y. Hishizawa, *Jpn. J. Appl. Phys.*, **27** (1988) L31.
- 15 S. Simizu, G. H. Bellesis, J. Lukin, S. A. Friedberg, H. S. Lessure, S. M. Fine and M. Greenblatt, *Phys. Rev. B*, in the press.
- 16 S. Simizu, private communication (1988).
- 17 B. D. Dunlap, M. Slaski, D. G. Hinks, L. Soderholm, M. Beno, K. Zhang, C. Segre, G. W. Crabtree, W. K. Kwok, S. K. Malik, I. K. Schuller, J. D. Jorgenson and Z. Sungalia, *J. Magn. Magn. Mater.*, **68** (1987) L139.