BNL-64616

International Conference on Neutron Scattering, Toronto, Canada, August 17-21, 1997

CONF-970814--

From double exchange to superexchange in charge ordering perovskite manganites

Wei Bao,[a] J. D. Axe,[a] C. H. Chen,[b] S-W. Cheong,[b] P. Schiffer,[c] and M. Roy[c]

[a] *Brookhaven National Laboratory, Upton, New York 11973, USA*

[b] *Bell Laboratories, Murray Hill, NJ 07974, USA*

[c] *University of Notre Dame, Notre Dame, IN 46556, USA*

Abstract

We found dynamic ferromagnetic correlations at the room temperature in perovskite manganites which have an antiferromagnetic insulating ground state. They are replaced by antiferromagnetic correlations when the electrons order. Our results indicate that the double exchange mechanism is turned off by electron localization at low temperatures.

Keywords: double exchange, colossal magnetoresistance, charge ordering, paramagnetic fluctuations

---

Metallic ferromagnetism in the mixed-valent manganites of perovskite structure, such as $La_{1-x}Ca_xMnO_3$ [1], can be understood by Zener's double exchange mechanism [2]. Theoretical calculations of the double exchange model predict ferromagnetic behavior for all doping with a maximum Curie temperature T_C at $x = 0.5$ [3]. In real materials, the ferromagnetic metallic phase occurs only around $x \sim 0.3$ [4] where most current research is concentrated due to the colossal magnetoresistance [5]. Outside this composition range, the ground state is insulating with various types of antiferromagnetic order [6]. Recently we discovered with neutron scattering that dynamic spin correlations are *ferromagnetic* at high temperatures for $Bi_{1-x}Ca_xMnO_3$ in composition range $0.74 \leq x \leq 0.82$ where the low temperature state is the C-type antiferromagnetic insulator [7].

Fig. 1 shows a composition-temperature phase diagram for $Bi_{1-x}Ca_xMnO_3$. It is similar to the phase diagram of $La_{1-x}Ca_xMnO_3$ in the overlapping composition range [8]. However, work reported here was made possible by our successful growth of single crystals in (Bi,Ca)MnO_3.

The resistivity ρ and the magnetic susceptibility χ are shown in Fig. 2(a) for a $x = 0.82$ sample. The ρ increases steeply below 210 K where the χ shows an inflection similar to that at a long range antiferromagnetic transition. However the Weiss constant Θ deduced from χ at high temperatures is positive and corresponds to a temperature marked in the figure where another anomaly occurs in χ. We showed with polarized neutron scattering that this lower temperature with a less conspicuous anomaly in χ is actually the Néel temperature for the C-type antiferromagnetic order [7], and the order parameter is shown in Fig. 2(b). At 210 K, where χ has a sharp turn, there is a charge ordering transition. The intensity of the superlattice peak as measured with electron diffraction is shown in Fig. 2(c). Concurrent with the charge ordering is a structural transition as evidenced by splitting of fundamental nuclear Bragg peaks (refer to open circles in Fig. 2(c)). Charge ordering and accompanying anomalies in thermodynamic properties have also been observed by us in $La_{1-x}Ca_xMnO_3$ ($x > 0.5$) [8].

We found [7] that above the charge ordering transition, the exchange interaction between

DISCLAIMER

spins is ferromagnetic. This shows up in ferromagnetic dynamic spin clusters which we were able to measure directly with neutron scattering. When charges order, which is also reflected in the steep increase of transport gap (refer to Fig. 2(a)), ferromagnetic exchange interaction is replaced by antiferromagnetic exchange. This is illustrated in Fig. 2(d) where the intensity of ferromagnetic spin clusters gives away to that of antiferromagnetic spin clusters. The latter condense to the long range antiferromagnetic order at 160 K in a conventional second order transition.

In summary, we found that the magnetic interaction is ferromagnetic at high temperatures for mixed-valent manganites with antiferromagnetic insulating ground state. This suggests that the double exchange mechanism is not limited to the finite composition range for the ferromagnetic metallic state. Charge localization and ordering at low temperatures, however, change the nature of magnetic exchange, which now is due to superexchange. The charge ordering resembles a freezing transition, therefore, electron localization may be driven by entropy.

We thank S. M. Shapiro, G. Shirane, C. Broholm, A. P. Ramirez, G. Y. Xu, P. Woodward, P. Littlewood, A. J. Millis, C. M. Varma, H. Y. Hwang, B. Batlogg for discussions. Work at BNL was supported by DOE under Contract No DE-AC02-76CH00016.

REFERENCES

[1] G. H. Jonker and J. H. Van Santen, Physica **16**, 337 (1950); J. H. Van Santen and G. H. Jonker, ibid. **16**, 599 (1950).

[2] C. Zener, Phys. Rev. **82**, 403 (1951); P. W. Anderson and H. Hasegawa, Phys. Rev. **100**, 675 (1955); P.-G. de Gennes, Phys. Rev. **118**, 141 (1960).

[3] C. M. Varma, Phys. Rev. B **54**, 7328 (1996); H. Roder, R. R. Singh and J. Zang, Los Alamos Cond-mat/9703146 (1996).

[4] J. B. Goodenough and J. M. Longon, in Landolt-Börnstein, New Series III, **4**, Pt a (Springer-Verlag, Berlin, 1970).

[5] S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and L. H. Chen, Science **264**, 413 (1994); S. Jin, H. M. O'Bryan, T. H. Tiefel, M. McCormack and W. W. Rhodes, Appl. Phys. Lett. **66**, 382 (1995).

[6] E. O. Wollan and W. C. Koehler, Phys. Rev. **100**, 545 (1955).

[7] W. Bao, J. D. Axe, C. H. Chen and S.-W. Cheong, Phys. Rev. Lett. **78**, 543 (1997).

[8] A. P. Ramirez, P. Schiffer, S-W. Cheong, C. H. Chen, W. Bao, T. T. M. Palstra, P. L. Gammel, D. J. Bishop and B. Zegarski, Phys. Rev. Lett. **76**, 3188 (1996); P. Schiffer, A. P. Ramirez, W. Bao and S-W. Cheong, Phys. Rev. Lett. **75**, 3336 (1995).

[9] H. Chiba, M. Kikuchi, K. Kusaba, Y. Muraoka and Y. Syono, Solid Stat. Comm. **99**, 499 (1996).

[10] J. B. MacChesney, H. J. William, J. F. Potter and R. C. Sherwood, Phys. Rev. **164**, 779 (1967).

FIGURES

FIG. 1. The composition-temperature phase diagram of $Bi_{1-x}Ca_xMnO_3$. Open symbols denote the charge ordering (CO) temperature. Solid symbols denote the Néel temperature. In this composition range, there are three types of long range magnetic order: the C-type antiferromagnet (AF-C), canted antiferromagnet (CNT) and the D-type antiferromagnet (AF-D). The circles are from single crystal studies [7], the squares from ceramic samples [9] and the diamond from [10].

FIG. 2. (a) Resistivity and magnetic susceptibility. The Weiss constant $\Theta = 158$ K. (b) Intensity of the magnetic Bragg peak (1/2,1/2,0). We use the pseudocubic perovskite unit cell in this paper. (c) Solid circles: intensity of the superlattice peak (0.11,0.11,0). Open circles: lattice constant of the pseudocubic cell. (d) Inelastic neutron scattering intensity from paramagnetic spin fluctuations, probing antiferromagnetic correlations at $\mathbf{q}$=(1/2,1/2,0) and $\hbar\omega = 1.7$meV (solid circles) and probing ferromagnetic correlations near the forward direction at $|\mathbf{q}| = 0.17\text{Å}^{-1}$ and 1 meV (open circles). The dotted line is background. See [7] for details.

Fig. 1, W. Bao et al. figures/sample/fig1.pro

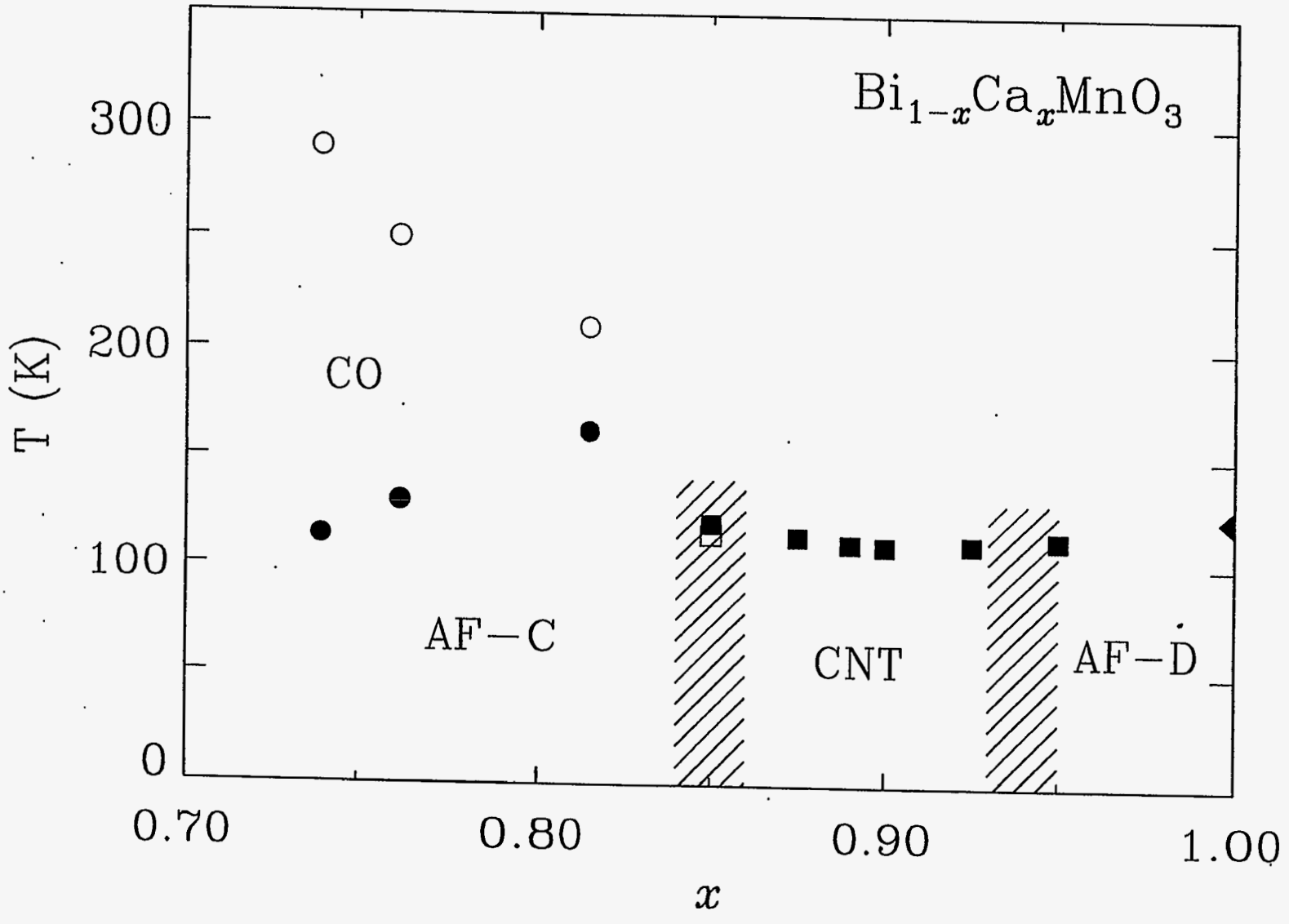

Fig. 2, W. Bao et al. fig2@~/tex/meeting/icm/icms.pro