Syposium on Magnetism in Metals
Copenhagen, Denmark, Aug. 26-29, 1996

Magnetism of Cuprate Oxides

By G. Shirane
Brookhaven National Laboratory
Upton, N. Y. 11973, U. S. A.

Synopsis
A review is given of the current neutron scattering experiments on cuprate oxides. We first discuss the extensive neutron measurements on high Tc oxides; La2-xSrxCuO4 and related (La1.6-xNd0.4)SrxCuO4. The second topic is the spin-Peierls system Cu1-xZnxCuO3, where a new type of antiferromagnetic phase has been discovered.

1 Introduction
It has been ten years since the discovery of high Tc superconductors by Bednorz and Müller. Very extensive neutron scattering studies have been carried out both on La2-xSrxCuO4 (214 type) and YBa2Cu3O6+δ (123 type). In this review, we limit our discussions only to the 214 type oxides and report some of the recent advances by the neutron scattering techniques.

The high Tc discovery prompted an extensive search for other copper oxides for new compounds of superconductivity. This resulted in opening a new field of magnetism not directly related to superconductivity. One of the most interesting copper oxides in this category is the spin-Peierls oxide CuGeO3, discovered by Hase et al. (1993). This oxide goes into the singlet dimer state below Tsp = 14K and is the first example of a simple oxide exhibiting a spin-Peierls transition. Again, the doping of Cu or Ge reveals very interesting phenomena, just like the doping of the high Tc oxides.

2 High Tc Oxides: La2-xSrxCuO4 Type
The antiferromagnetic spin fluctuations in these copper oxides have been studied extensively and a review was given by Shirane et al. (1994). The double peaks in q scan across the 2D ridge was first reported by Birgeneau et al. (1989) and the exact locations of satellite peaks were later mapped out by Cheong et al. (1991). Despite extensive neutron scattering studies of La0.85Sr0.15CuO4, the existence of energy gap in magnetic excitation spectrum has only been demonstrated very recently (Yamada et al. 1995).
The progress of the neutron scattering study of high Tc oxides has always been dictated by the successful crystal growth of better (and larger) crystals. The latest step along this line for La$_{0.85}$Sr$_{0.15}$CuO$_4$ was accomplished by Hosoya et al. in 1994. These crystals are called Sendai, where they were grown, and they show the highest onset of T$_c$ at 37.3K. Improved quality of the crystals is also reflected in the sharp phase transition between orthorhombic and tetragonal phases. Very recently, Yamada et al (1996) extended the study for a wide range of x in La$_{2-x}$Sr$_x$CuO$_4$. These very interesting experimental results are discussed extensively by Y. Endoh in this conference. Thus, we limit ourselves only to the special topics related to the incommensurate peaks around $(\pi, \pi)$ position.

The neutron data shown in Fig. 1 were taken with a large (1.5cc) and nearly perfect single crystal. In contrast to the results reported on lower T$_c$ crystals, the intensity below 3.5 mev dramatically decreases as the temperature decreases below T$_c$ and vanishes into the background below 15K. The clear cut gap is observed only at the optimal doping x = 0.15 with $\delta = 0.12$. The important relation between $\delta(x)$ and T$_c$ is discussed by Endoh.

1/8 problem

One of the long-standing puzzles in high Tc research is depicted in Fig. 2. An amazing dip of T$_c$ vs composition in La$_{2-x}$Ba$_x$CuO$_4$ was discovered by Moudenbaugh et al. in 1988. Axe et al. (1989) then demonstrated that this dip is related to the phase transition from the low temperature orthorhombic (LTO) to low temperature tetragonal (LTT) structure. It is not possible to grow large enough single crystals of La$_{2-x}$Ba$_x$CuO$_4$ to study this feature, but crystals are available for La$_{2-x-y}$Nd$_y$Sr$_x$O$_4$, which exhibits a similar dip in T$_c$ as a function of x. This is called 1/8 problem because the dip in T$_c$ (See Fig. 2) corresponds to the x value of 1/8.

Very recently Tranquada et al. (1995) have carried out an elegant and comprehensive neutron scattering experiments on La$_{1.48}$Nd$_{0.4}$Sr$_{0.12}$CuO$_4$. Their key results are shown in Fig. 3, which also depicts the scattering geometry. Incommensurate dynamical spin correlations have been known in La$_{2-x}$Sr$_x$CuO$_4$ (see Fig. 1) for sometime. What is new in Fig. 3 is that these magnetic peaks at $\delta$ are elastic Bragg peaks. Moreover, the 2$\delta$ peak is observed around (200), (tetragonal notation) and this represents the charge modulation. The LTT structure plays the key role for this special type of stripe phase (see Fig. 4).

This development of the charge density wave (CDW) is the cause of depression of T$_c$. The phase transition from LTO to LTT phase occurs at 70K. The transition to the CDW phase takes place around 60K, which is 10°K higher than the magnetic transition near 50K. In this system, the phase transition is driven by charge and it is quite different from the case of Cr.
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
when the charge part is the secondary effect of the spin ordering. Further study of these fascinating phase transitions continues.

3 Doped Spin Peierls System Cu(Zn)GeO₃

The spin Peierls (SP) transition in CuGeO₃ at \( T_{sp} = 14K \) was discovered by Hase et al. in 1993. Previous examples of spin-Peierls were all organic compounds and this simple inorganic oxide, gives us the first chance for full understanding of the detailed mechanism of the phase transition into a singlet state mainly because large single crystals can be produced. Comprehensive measurements have already been carried out on important physical properties of CuGeO₃; energy gap and magnetic excitations by Nishi et al. (1994) dimerized atomic configuration by Hirota et al. (1994). The structure below 14K is the simple combined displacements of coppers and oxygen to form alternate dimers in the crystal.
Immediately after the discovery of CuGeO₃, the effect of substitution of Zn for Cu was reported by Hase et al. (1993). Then followed several papers on Cu(Zn) and Ge(Si) doping. I shall discuss in some detail our current neutron scattering studies at Brookhaven on Zn doped CuGeO₃. This topic may be somewhat out of place for a conference on Magnetism in "Metals", but the coexistence of antiferromagnetic (AF) order with spin-Peierls dimerization is a new and exciting physics, which may have future implications on other branches of magnetism and phase transitions. From measurements on powder samples, it is now well established that a new AF ordered phase appears as shown in the phase diagram of Fig. 5. The SP transition is near 14.2K for the undoped oxide, decreases in temperature with increased Zn concentration, and seemed to disappear around 2% Zn. At 4% Zn, the magnetic susceptibility no longer shows a SP transition, but only a Néel temperature Tₙ ~ 4K.
A very surprising result was then reported by Regnault et al. (1995) in their neutron scattering study of 0.7% Si-doped CuGeO₃. As shown in Fig. 6, Regnault et al. demonstrated the successive SP (9K) and AF(4K) transitions with two separate branches of magnetic excitations below $T_N$. Note that the dimer peak $\frac{1}{3} - \frac{1}{2}$ decreases below $T_N$ but does not disappear. The co-existence of the SP and AF state was first demonstrated in this work. The coexistence of two order parameters, in this fashion, is extremely rare in structural and magnetic phase transitions.

The phase diagram of doped Cu(Zn)GeO₃ was re-examined by Sasago et al. (1996) and, as shown in Fig. 7, the co-existence of AF and SP phases is also demonstrated in this system. As shown in the inset of Fig. 5, the $T_{sp}$ at 10K in Zn 4% sample does not reveal itself in the magnetic susceptibility measurement. However, this is clearly seen in neutron scattering by the appearance of the dimer line $\frac{1}{2} - \frac{1}{2}$ in Fig. 7.

The SP transition persists up to nearly 5% Zn concentration. Fukuyama et al. (1996) proposed a theoretical model for antiferromagnetic order in disordered spin-Peierls systems. They suggest that, surprisingly, long range lattice distortions will actually enhance the degree of the long range coherence of the antiferromagnetism. This model is quite different from the conventional "percolation" type idea in which islands of activated AF copper moments...
Fig. 7. Intensities of the SP and AF superlattice peaks as functions of temperature for a 3.2% Zn-doped crystal. The intensity of the SP lattice dimerization peak is seen to decrease below $T_N$, however the states are clearly coexisting. The inset shows $T_{SP}$ and $T_N$ measured on samples of 0.0, 0.1, 0.2, and 0.4% Zn-doped crystals. After Sasago et al. (1996).

around Zn dopants eventually form "connected" AF order. Fukuyama et al. proposes explicit shape of both order parameters (Cu moment and dimer shift) as a function of dopant concentration. A particularly intriguing question is the lowest limit of concentration $x$ for the appearance of the AF phase. This problem is now being pursued by Martin et al. (1996): they recently observed a long range AF peak below 0.6K for Zn concentration of 0.4%. It is rather unbelievable that such a small concentration of Zn substitution does create true long range magnetic order. The phase diagram of the Cu$_{1-x}$Zn$_x$GeO$_3$ system is constructed by Martin et al. (1996) and shown in Fig. 8. The data combined both neutron and susceptibility measurements. How about the magnetic excitations? Regnault et al. (1995) reported the existence of separate low energy extensions in small $q$ regions from AF peak $(01 \frac{1}{2})$. Extensive neutron scattering measurements are now being carried out by Martin et al. (1996) and they have extended AF mode measurements to much wider range in $q$ space. Further neutron scattering studies are needed to complete the picture of this fascinating system.

Acknowledgment

I would like to thank my collaborators for the stimulating discussions, in particular, R. J. Birgeneau, Y. Endoh, V. J. Emery, H. Fukuyama, M. Hase, K. Hirota, Y. Sasago, J. M. Tranquada, K. Uchinokura, and K. Yamada. This work was supported in part by the U.S. Japan collaboration on Neutron Scattering.
and NEDO International Research grant. Research at Brookhaven was carried out under contract No. DE-AC02-76CH00016, Division of Materials Science, U. S. Department of Energy.
REFERENCES


FIGURE CAPTIONS

Fig. 1. Neutron inelastic scattering spectra at 3meV for Sendai crystal 1 at T = 40K (>Tc) (a) and T = 4K (b) taken by scan A. At the top is a schematic drawing of reciprocal space near the (π, π) position; typical scan directions are denoted by A, A', B, and B'. The closed circles denote the peak positions of the incommensurate magnetic fluctuations. In the [H H] zone, scans A and B can be performed with tilts of the crystal around the c* axis equal to 6° and 10°, respectively. After Yamada et al. (1995).

Fig. 2. Phase diagram of La_{2-x}Sr_{x}CuO_{4} (solid line). AF denotes antiferromagnetic order and SC indicates superconductivity. Dashed line indicates the superconducting regime in La_{2-x}Ba_{x}CuO_{4}.

Fig. 3. Elastic scans with 2.4 Å neutrons of superlattice peaks consistent with the proposed spin and charge stripes, in La_{1.48Nd_{0.45}Sr_{0.37}CuO_{4} at 11K. (a) Diagram of the (b0l) zone of reciprocal space. Open circles indicate locations of Bragg peaks for the LTT structure; solid circles denote spin- and charge-ordering superlattice peaks. Arrows indicate the regions scanned. (b) Scan along (1/2,1/2 + q, 0) through the (1/2, 1/2 ± ε, 0) peaks. The small peak width indicates that the in-plane correlation length is greater than 150 Å. (c) Scan along (0,2, q, 0) through the (0,2, -2 ε, 0) peak. The lines in (b) and (c) are the result of least-squares fits to gaussian peak shapes plus a flat background. After Tranquada et al. (1995).

Fig. 4. (a) Sketch of the (b0l) zone of the reciprocal lattice showing the positions of the magnetic scattering peaks observed for hold-doped La_{2}CuO_{4} (filled circles) and La_{2}NiO_{4} (open circles). (b) Idealized diagram of the spin and charge stripe pattern within an NiO_{2} plane observed in hole-doped La_{2}CuO_{4} with n_{h} = 1/4. (c) Proposed stripe pattern in a CuO_{2} plane of hole-doped La_{2}CuO_{4} with n_{h} = 1/8. In both (b) and (c), only the metal atoms are represented; the oxygen atoms, which surround the metal sites in a square planar array, have been left out. After Tranquada et al. (1995).

Fig. 5. The previously reported phase diagram for Cu_{1-x}Zn_{x}GeO_{3} as deduced from magnetic susceptibility measurements of powders. The inset shows the susceptibility measurement of an x = 0.04 single crystal in the a, b and c crystallographic directions as labeled. After Hase et al (93,95).
Fig. 6. Temperature dependencies of elastic contributions at scattering vectors (a) $Q = (1/2, 3, 1/2)$ and $Q = (0, 1, 1/2)$ and (b) $Q = (0, 1, 0.25, 1/2)$, showing the occurrence of an antiferromagnetic phase transition at $T_N = 4K$. After Regnault et al. (1995).

Fig. 7. Intensities of the SP and AF superlattice peaks as functions of temperature for a 3.2% Zn-doped crystal. The intensity of the SP lattice dimerization peak is seen to decrease below $T_N$, however the states are clearly coexisting. The inset shows $T_{SP}$ and $T_N$ measured on samples of 0, 0.9, 2.1, 3.2, and 4.7 percent Zn-doped crystals. After Sasago et al. (1996).

Fig. 8. The current phase diagram of Cu(Zn)GeO$_3$ constructed by Martin et al. (1996) for neutron and susceptibility measurements.