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NEUTRON SCATTERING STUDIES OF MAGNETISM IN THE HIGH-T_c MATERIALS

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In this paper, I shall attempt to review what has been learned about magnetism in the high-T_c family of compounds using neutron scattering techniques. Whether or not it is true that magnetic effects are involved in an essential way in the mechanism for superconductivity in these materials (a point which has not yet been firmly established), they offer fascinating examples for the study of magnetism for its own sake, being realizations of spin 1/2 2D quantum antiferromagnets. Further, the rare earth spins in these materials also order at low temperatures reminiscent of the coexistence of antiferromagnetism and superconductivity in the earlier well-studied families of magnetic superconductors such as $ErRh_4B_4$ and the Chevrel-phase compounds[1], with the difference that the ordering here is primarily 2D in character.

In spite of early predictions that the Neel state in La_2CuO_4 might be pre-empted in favor of a spin-liquid like (RVB) state[2], La_2CuO_4 was found by powder neutron diffraction to be an antiferromagnetic insulator[3], in common with many other transition metal oxides. The most likely interpretation is that the undoped parent compounds of these materials are realizations of Mott-Hubbard insulators, the nearest neighbor antiferromagnetic exchange interaction J being given by $J \sim t^2/4u$, t being the effective Cu-Cu hopping matrix element (via the oxygens) and U being the Coulomb repulsion between the holes on the Cu^{2+} ions. The by now well-known 3D antiferromagnetic (AF) structure of La_2CuO_4 is shown in Fig. 1, where only the Cu atoms are shown for simplicity. The crystal structure in this phase is orthorhombic. (We shall keep the original Cmca space group notation for the axes as denoted in Fig. 1.) Thus the lattice constant a is slightly different from c. As seen in Fig. 1, if it were not for this fact, the coupling of a Cu spin to its nearest neighbors in adjacent CuO_2 planes would be completely frustrated as J_1 would be = J_2. This cancellation can be broken by the orthorhombic distortion and also by magnetic dipole-dipole coupling, resulting in a very weak interplanar exchange coupling between CuO_2 AF layers (4-5 orders of magnitude less than the in-plane nearest neighbor exchange J_O). Thus the primary ordering in these systems is two-dimensional, within the CuO_2 planes. However, a 2D spin system cannot order (even classically) except at T=0 so that true long-range order is achieved only when the 2D correlation length has become large enough that even the tiny interplanar coupling can induce ordering at a temperature given from energy considerations, by

$$kT_N \approx J'(M/M_0)^2(\xi/a)^2 \qquad (1)$$

where ξ is the 2D correlation length in the planes, a is a typical lattice constant, J' the effective interplanar exchange coupling and (M/M_O) is the staggered magnetization relative to the Neel value. The 2D short range correlations were first studied in La_2CuO_4 by Birgeneau, Shirane and coworkers at Brookhaven[4] using single crystals grown by the flux technique and without energy analysis, i.e. intergrating over the scattered neutron energies. They found that the 2D correlations persisted to

well above T_N with a temperature dependent correlation length which is shown in Fig. 2. Around the same time, Chakravarty, Halperin and Nelson (CHN) had given theoretical arguments for mapping the 2D spin 1/2 quantum Heisenberg model on to a 3D classical rotator model, the so-called non-linear sigma model (NLσM), and solved the latter problem via renormalization group techniques[5]. They arrived at the conclusion that for much of parameter space, a quantum spin 1/2 Heisenberg antiferromagnet behaved very similarly to a classical 2D Heisenberg antiferromagnet with renormalized parameters, involving long-range order at T=0 and a correlation length which behaves like

$$\xi = C\exp(2\pi\ \rho_s / k_B T) \qquad (2)$$

where C is a constant ~ 0.4, a the nearest neighbor distance and ρ_s is the spin stiffness constant at T=0. Fig. 2 shows that this expression fits the experimental data reasonably well, the spin-wave stiffness being the value obtained from inelastic neutron scattering measurements on La_2CuO_4. Inelastic neutron scattering measurements have also studied the magnetic excitations in La_2CuO_4. The measurements are difficult because of the steepness of the "spin-wave cone" emanating from the rods in reciprocal space which are normal to the CuO_2 planes and pass through the AF reciprocal lattice points. They require "hot neutrons" and constant energy scans at large energy transfers to resolve the peaks on either side of the rod, such as have been carried out by Aeppli et al.[6]. These experiments yield good agreement with a damped spin-wave model and a spin-wave velocity of 0.85 eVÅ, corresponding to a nearest neighbor in-plane exchange constant J_0 of 0.16eV. The low energy excitations or $S(Q,\omega)$ in La_2CuO_4 above the 3D Neel temperature are also in good agreement with the theory of CHN when allowance is made for instrumental resolution[7]. Thus even though the mapping of the NLσM on to the 2D spin 1/2 Heisenberg antiferromagnet may not satisfy theorists insistent on rigorous proofs, it appears that within the accuracy of the experiments, we have a quantitative understanding of both the statics and the dynamics of the 2D quantum Heisenberg antiferromagnet.

Similar 3D antiferromagnetic structures have been found for the compounds La_2NiO_4[8], (S=1), La_2CoO_4[9], (S=3/2), Nd_2CuO_4[10] and Pr_2CuO_4[10]. The basic long-range order in the CuO_2 planes is identical in all the copper oxide compounds (including the 123 family), it is only the 3D stacking of the AF layers that varies, since it is governed by the weak interplanar coupling. Whether the 3D magnetic wavevector is regarded as propagating along the [100] or [001] direction in the basal plane (in the Cmca notation) is in fact fixed by the 3D stacking sequence. Thus in La_2NiO_4 this stacking sequence is opposite in sense to that in La_2CuO_4, or alternatively q_m is directed parallel to the ordered spin direction rather than normal to it as in La_2CuO_4 (Fig. 1). For La_2CoO_4 the ordering at T_N is of the La_2NiO_4 type and then at lower temperatures switches to the La_2CuO_4 type as the structure becomes tetragonal. The compound $Sr_2CuO_2Cl_2$ which is similar to La_2CuO_4 except for the replacement of La^{3+} ions by Sr^{2+} ions and of the apical oxygens by Cl ions, is always tetragonal but is nevertheless found to exhibit long-range 3D order with T_N=251K[11]. In this case the interplanar frustration is probably broken by magnetic dipole-dipole coupling rather than superexchange between layers, which favors the La_2CuO_4 structure which is observed. Fig. 3

shows the antiferromagnetic superlattice intensity for these compounds as a function of temperature. It does not show the normal saturated behavior at low T characteristic of 3D antiferromagnets, because it is much more 2D in nature, the interplanar coupling being ~10^{-6} J_o instead of 10^{-4} J_o as in La_2CuO_4[11] and thus the staggered magnetization decreases as $T\ell nT$ rather that T^2. The extremely weak interplanar coupling makes the high value of the 3D T_N somewhat of a puzzle, since it would imply an in-plane correlation length much larger than the 2D Heisenberg spin 1/2 model predicts at T_N (see Eqs. (1) and (2)). Birgeneau[11,12] has speculated that in this compound (and also in the tetragonal compounds Nd_2CuO_4 and Pr_2CuO_4) there is a crossover to 2D x-y model behavior above T_N. It would thus be quite interesting to study the 2D spin-correlations in detail in $Sr_2CuO_2Cl_2$ when large enough single crystals are available in order to study a possible quantum 2D x-y magnetic transition.

The compounds Nd_2CuO_4 and Pr_2CuO_4 are interesting in the sense of being the parent compounds of the so-called "electron doped" superconductors. They stay tetragonal all the way down to low temperature. Pr_2CuO_4 has the La_2CuO_4-type AF structure[10] with changes in superlattice reflection intensities being well-accounted for by a Pr^{3+} moment which follows the Cu^{2+} ordered moment according to the law

$$\langle \mu_{Pr} \rangle = \chi_{ab} \; J \langle \mu_{Cu} \rangle \qquad (3)$$

χ_{ab} being the in-plane paramagnetic single-ion susceptibility of the Pr^{3+} ion and J being the magnitude of the Pr-Cu (weak) exchange interaction. The excellent agreement of this model with experiment indicates very little Pr-Pr interaction. On the other hand, Nd_2CuO_4 shows more complicated behavior[10]. At T_N (255K), the Cu spins order in a La_2NiO_4 structure. However at lower temperatures they reorient to the La_2CuO_4 structure and at still lower temperatures rotate again, accompanied by Nd^{3+} spin ordering, which also indicate interactions between the Nd spins. 2D spin correlations above T_N are found in both compounds.

Fig. 4 shows the AF spin structure found in $YBa_2Cu_3O_6$[13]. The basic AF Cu-O planes are coupled antiferromagnetically as bilayers with a weaker coupling between bilayers through the planes containing the Cu1 sites ("chain sites"). Inelastic spin-wave measurements have been carried out both below and above T_N[14]. The bilayer AF correlations persist to well above T_N in these materials. The stacking between the bilayers appears to be sensitive to sample impurities and/or the rare earth ions which might replace Y, especially upon doping with oxygen. The phase diagram as a function of oxygen doping was measured by Tranquada et al.[13]. Similar results have been obtained by the Grenoble group[15]. Oxygen introduces holes into $YBa_2Cu_3O_{6+x}$, but T_N does not initially drop as rapidly as it does with hole doping in $La_{2-x}Sr_xCuO_4$. This is presumably because the oxygens go into the chain-sites in the Cu1 planes and initially convert the non-magnetic Cu^{1+} ions in those sites to magnetic ions. This sets up some frustration in how these are to order, which may account for the variety of structures (and even disorder) between bilayers seen in these compounds and $NdBa_2Cu_3O_{6+x}$ samples for example[16-18]. Howeverm further oxygen doping

starts putting holes into the Cu-O planes containing the Cu_2 sites and T_N then drops extremely rapidly reaching zero at about x=0.4.

The introduction of holes in all of these compounds thus destroys the AF correlations in the Cu-O planes, as also evidenced directly by neutron scattering measurements of the correlation length in the doped antiferromagnets. The Brookhaven-MIT Group have studied the behavior of ξ with x in $La_{2-x}Sr_xCuO_4$. The 2D correlation length (which rapidly becomes temperature independent with doping) decreases approximately as the average spacing between holes[4]. Correspondingly as one can see from Eq. (1), the 3D ordering temperature drops and eventually gives rise to a spin-glass phase.

The 2D correlations have also been measured in the Ce-doped Pr_2CuO_4 and Nd_2CuO_4 compounds[19] where it appears that the effect of electron doping is not as catastrophic on the AF order as that of hole-doping. Presumably this is because electron doping simply removes the spin on the Cu^{2+} ions causing dilution rather than the frustration caused by holes on the O sites with their strong exchange interaction between neighboring Cu spins. The latter is probably responsible[20] for the "spin-glass" phase found in $La_{2-x}Sr_xCuO_4$ at low temperatures beyond x=0.06[21].

Interestingly, though, while the magnetic scattering broadens considerably in q-space (due to shorter correlation lengths) the integrated magnetic intensity persists almost unchanged even in the superconducting phases, implying that the Cu spins persist also. With the results of many experiments on both the 214 and 123 family of compounds, it is at this stage unlikely that all the magnetic scattering in the superconducting phase could be explained by coexisting magnetic and non-magnetic (superconducting) phases. Thus one is led to the conclusion that at least short range 2D magnetic correlation are an intrinsic part of the superconducting ground state at least for the lower-doping sides of the phase diagrams. Inelastic neutron scattering measurements are consistent with a softening of the spin-wave velocity at least for low (non-superconducting) dopant levels. For a sample of $La_{2.89}Sr_{0.4}CuO_4$, measurements at Brookhaven[22] yield a somewhat puzzling set of peaks in constant energy scans where the q-positions move out from the reciprocal lattice point with increasing energy transfer and then back in again at still higher energy transfers. This could be due to the existence of spin-wave cones originating from incommensurate reciprocal lattice points, but this has not yet been rigorously demonstrated. Shirane et al. also find a rapid decrease in scattered intensity below 100K for energy transfers below 6 meV in a Tc=33K sample of $La_{1.85}Sr_{0.15}CuO_4$[23] while no such decrease appears at higher energy transfers. They interpret this as evidence of a gap opening up. However, the $\chi''(Q,\omega)$ extracted from $S(Q,\omega)$ by correcting for the detailed balance factor $[1- e^{-\beta\omega}]^{-1}$ does not look as convincing with regard to the existence of such a gap. For the $YBa_2Cu_3O_{6+x}$ systems the Brookhaven group has carried out inelastic neutron scattering studies for concentrations of x upto 0.5 (Tc=50K)[24]. They find that their results can be well represented by the form

$$S(\vec{q},\omega)=\frac{\hbar\omega}{1-e^{-\beta\omega}}\frac{A}{\kappa^2+q^2}\left[\frac{\Gamma}{\left(\hbar\omega-\hbar\omega_q\right)^2+\Gamma^2}+\frac{\Gamma}{\left(\hbar\omega+\hbar\omega_q\right)^2+\Gamma^2}\right] \quad (4)$$

as expected for the scattering from a system of spins processing only paramagnetic short-range order. Note that the scattering is peaked at non-zero energy transfers because of the damping Γ and not because of the existence of a gap. In this respect, these authors differ in their conclusions from the Grenoble group[25]. This is obviously an important question which will require much careful future study.

We conclude with a discussion of some other issues relating to the magnetism which have yet to be resolved. One is the question of the ordered moment in the 3D ordered structures. For the samples with the highest T_N (300K for La_2CuO_4 and 500K for $YBa_2Cu_3O_6$) the saturated ordered moment per Cu atom is ~0.5μ_B which compares well with the 0.6μ_B predicted by spin-wave theory for a quasi-2D spin 1/2 antiferromagnet[26]. However, if the oxygen stoichiometry is changed, both T_N and the ordered moment drop drastically, as measured by neutrons. μSR measurements, on the other hand, which probe only static local (rather than long-range global) magnetic moments do not show a drastic decrease in the ordered Cu moment[27]. Thus there appear to exist regions of increasing disorder brought about by oxygen doping. In any case, we have as yet no clearly accepted theory of how the presence of static or even itinerant holes affects the ordered moment in a quantum antiferromagnet, although Maleev has presented at this conference[28] some interesting new thoughts on this question. The other has to do with the question of the oxygen ions: what is the nature of the covalent bond between the Cu and the O ions in the presence of strong correlations, and if so how does it affect the spins on the Cu sites? Fig. 5 shows the antiferromagnetic form factors of La_2CuO_4 and $Sr_2CuO_2Cl_2$ measured by Stassis et al.[29] which shows that a simple Cu^{2+} spin form factor does not fit the data. On the other hand, a simple phenomenological model where one puts 10% of the Cu spin on the O site, (with the O spin density having a dipolar form, pointing parallel to each Cu spin on the appropriate side of the O ion) fits the observed form factor rather well. This can be explained in terms of a small mixing of the spin-polarized Cu d-orbitals with their neighboring O p-orbitals, or covalency effects. If one measures the form-factor of induced magnetization in an externally applied magnetic field however, as has been done for La_2CuO_4[30], one finds very little spin polarization on the O site, contrary to the predictions of band-structure theory or intuitive ideas about covalent bonding.

I have discussed here results many of which were carried out not by myself but by my colleagues at Brookhaven and other places. I thank them for their helpful discussions and permission to discuss their results, particularly J. Tranquada, G. Shirane, R.J. Birgeneau, and C. Stassis. I also wish to acknowledge and thank many collaborators, particularly D. Vaknin, D. Johnston, and C. Stassis.

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References:

1. "Superconductivity in Ternary Compounds", O. Fischer & S.D. Baeler (Eds.), Springer 1981.
2. P.W. Anderson, Science 235, p. 1196 (1987).
3. D. Vaknin, S.K Sinha, D.E. Moncton, D.C. Johnston, J.M. Newsam, C.R. Safinya, H.E. King Jr., Phys. Rev. Lett. 58, p. 2802 (1987).
4. R.J. Birgeneau and G. Shirane, in "Physical Properties of High-temperature Superconductors" (Ed. D.M. Ginsberg), World Scientific Publishing (1989); Y. Endoh et al., Phys. Rev. B37, p. 7443 (1988).
5. S. Chakravarty, B.I. Halperin, D.R. Nelson, Phys. Rev. Lett. 60, p. 1057 (1988); Phys. Rev. B39, p. 2344 (1989).
6. G. Aeppli, S.M. Hayden, H.A. Mook, Z. Fisk, S.-W. Cheong, D. Rytz, J.P. Remeika, G.P. Espinosa, A.S. Cooper, Phys. Rev. Lett. 62, p. 2052 (1989).
7. K. Yamada et al., Phys. Rev. B40, p. 4557 (1989).
8. G. Aeppli and D.J. Buttrey, Phys. Rev. Lett. 61, p. 203 (1988).
9. K. Yamada, M. Matsuda, Y. Endoh, B. Keimer, R.J. Birgeneau, S. Onodera J. Mizusaki, T. Matsuura, G. Shirane, Phys. Rev. B39, p. 2336 (1989).
10. M. Matsuda et al., Phys. Rev. B (1990) to be published; S. Skanthakumar and J. W. Lynn, Physica C170, p. 175 (1990).
11. D. Vaknin, S.K. Sinha, C. Stassis, L.L. Miller, D.C. Johnston, Phys. Rev. B41, p. 1926 (1990).
12. R.J. Birgeneau, Private communication;
13. J.M. Tranquada et al., Phys. Rev. Lett. 60, p. 156 (1988); J.M. Tranquada et al., Phys. Rev. B38, p. 2477 (1988).
14. J.M. Tranquada, G. Shirane, B. Keimer, S. Shamoto, M. Sato, Phys. Rev. B40, p. 4503 (1989).
15. J. Rossat-Mignod, P. Burlet, M.J. Jurgens, J.Y. Henry, C. Vettier, Physica C153, p. 19 (1988), and J. Rossat-Mignod, these proceedings.
16. H. Kadowaki, M. Nishi, Y. Yamada, H. Takeya, H. Takei, S.M. Shapiro, G. Shirane, Phys. Rev. B37, p. 7932 (1988).
17. A.H. Moudden, G. Shirane, J.M. Tranquada, R.J. Birgeneau, Y. Endoh, K. Yamada, Y. Hidaka, T. Murakami, Phys. Rev. B38, p. 8720 (1988).
18. J.W. Lynn, W-H. Li, H.A. Mook, B.C. Sales, Z. Fisk, Phys. Rev. Lett. 60, p. 2781 (1988).
19. T.R. Thurston, et al., Phys. Rev. Lett. 65, p. 263 (1990).
20. A. Aharony, R.J. Birgeneau, A. Coniglio, M.S.Dastner, H.E. Stanley, Phys. Rev. Lett. 60, p. 30 (1988); R.J. Birgeneau, M.A. Kastner, A. Aharony, Phys. Rev. B71, p. 57 (1988).
21. J.L. Budnick et al., Europhys. Lett. 5, p. 651 (1988); D.R. Harshman et al., Phys. Rev. B38 p. 852 (1988); Y.J. Uemura et al., J. Physique C8, p. 2087 (1988).
22. T.R. Thurston,et al., Phys. Rev. B.40, p. 4585 (1989).
23. G. Shirane et al., Phys. Rev. Lett. 63, p. 330 (1989).
24. J.M. Tranquada, W.J.L. Buyers, H. Chou, T.E. Mason, M. Sato, S. Shamoto, G. Shirane, Phys. Rev. Lett. 64, p. 800 (1990).
25. J. Rossat-Mignod, these proceedings.
26. D.A. Huse, Phys. Rev. B37, p. 2380 (1988); J.D. Reger and A.P. Young, Phys. Rev. B37, p. 5978 (1988).
27. Y.J. Uemura et al., Phys. Rev. Lett. 59, p. 1045 (1987).
28. S.V. Maleev, these proceedings.
29. T. Freltoft et al., Phys. Rev. B37, p. 137 (1988); X.L. Wang, C. Stassis, D.C. Johnston, C.-K. Loong, B.N. Harmon, to be published.
30. C. Stassis, B.N. Harmon, T. Freltoft, G. Shirane, S.K. Sinha, K. Yamada, Y. Endoh, Y. Hidaka, T. Murakami, Phys. Rev. B38, p. 9291 (1988).

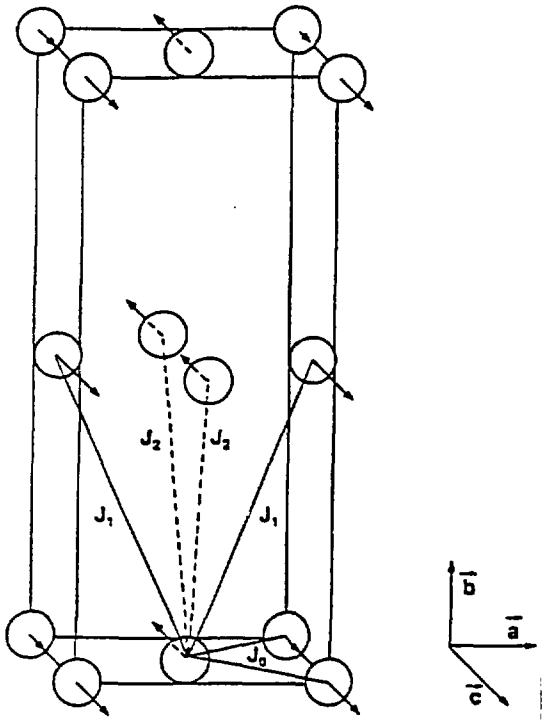
Fig. 1 The 3D antiferromagnetic structure of La_2CuO_{4-y}. Only the Cu atoms are shown. J_0, J_1, J_2 represent the in-plane and out-of-plane nearest neighbor exchange interactions respectively. The unit cell axes in the Cmca notation are shown. (from Ref. /3/)

Fig. 2 Inverse correlation length versus temperature in La_2CuO_4 in a crystal with T_N=195K. The solid line is the theoretical prediction of Ref. /5/. (from Ref. /4/)

Fig. 3. Intensity of the (1/2,1/2,0) magnetic superlattice reflection versus temperature for $Sr_2CuO_2Cl_2$. (from Ref. /11/)

Fig. 4. 3D antiferromagnetic structure of $YBa_2Cu_3O_{6+x}$. The 01 sites are empty for x=0.

Fig. 5 The antiferromagnetic form factors of La_2CuO_4 and $Sr_2CuO_2Cl_2$. The solid curve is the free ion Cu^{2+} form factor. (from Ref. /29/)



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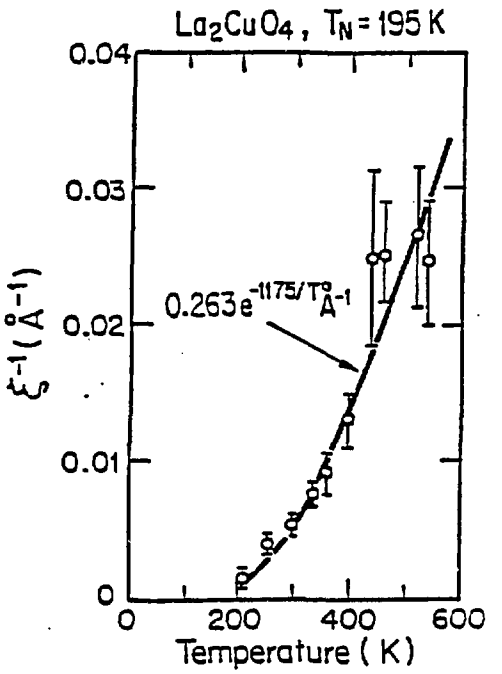

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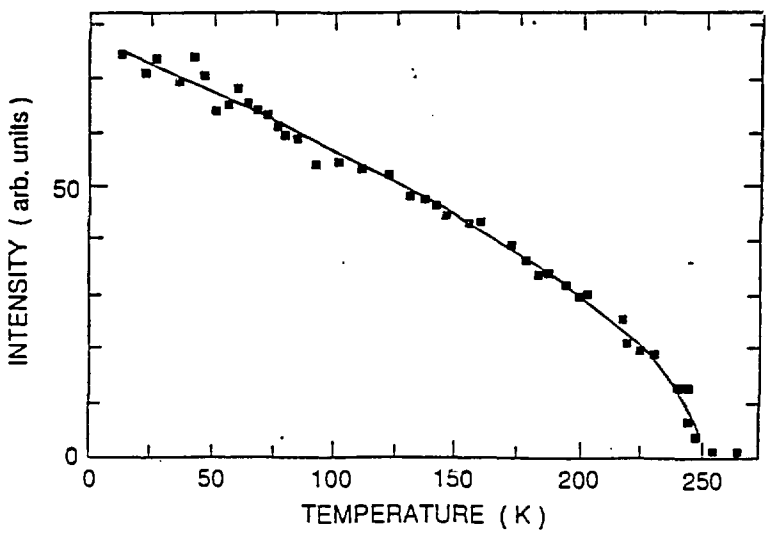

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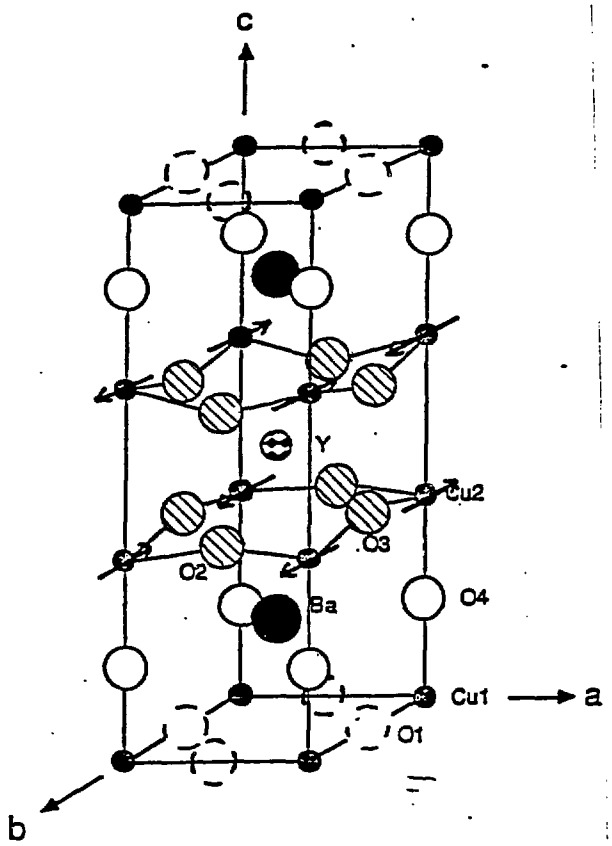

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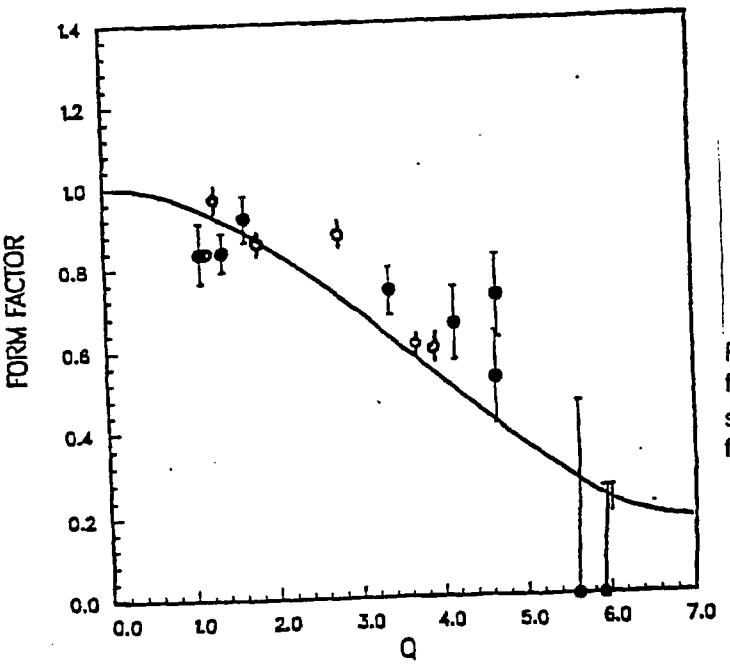

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