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Effect of transition-metal elements on the superconductivity of Y-Ba-Cu-O

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We have fabricated samples of the form $YBa_2(Cu_{0.9}A_{0.1})_3O_{6+y}$, where A = Ti, Cr, Mn, Fe, Co, Ni, Cu, and Zn. The superconducting state was investigated by both resistance and magnetization measurements. In addition, the magnetic susceptibility above T_c has been measured. T_c was found to be strongly correlated with the size of the paramagnetic moments, largely due to scattering from the magnetic sites. In the sample containing Zn, however, T_c was dramatically reduced due to filling of the antibonding *d* band.

Recently, the structure and composition of the single phase responsible for the high transition temperature ($T_c = 94$ K) superconductivity in the Y-Ba-Cu-O system has been determined.[1,2] The structure is a cuprate perovskite with composition $YBa_2Cu_3O_{6+y}$ (the 1-2-3 compound). Interestingly, the superconductivity remains essentially unaffected by the substitution of Y with isoelectronic rate-earth elements that have a large localized magnetic moment.[3] This has led to the conclusion that the superconductivity in this class of materials is confined to the CuO_2-Ba-CuO_2 layer assembly.[3] In addition, the expected local density of states at the Fermi level, DOS(E_F), should be small around the Ba^{2+} and Y^{3+} sites because of the stable Xe and Kr core electron structure. Thus, the main contribution to the DOS(E_F) comes from the Cu *d* band and the *spd* hybridization states due to the Cu and O ions. Substitution of Cu with metallic elements should produce substantial changes in the superconducting properties which in turn allows the nature of the high-T_c superconductivity and electronic structure to be elucidated.

The ionic size and orbital structure of the 3*d* elements are close to those of Cu; we expect that the 3*d* elements will occupy the Cu sites if they are substituted into the 1-2-3 structure. We have taken the 1-2-3 system and performed a systematic substitution of the 3*d* elements for 10% of the Cu ions. The samples are represented by $YBa_2(Cu_{0.9}A_{0.1})_3O_{6+y}$, where A = Ti, Cr, Mn, Fe, Co, Ni, and Zn. This level of substitution provides a sizable change in T_c in each case, but is not large enough to destroy superconductivity. A strong correlation between superconductivity and the electronic and magnetic behavior of the substituting elements has been observed.

All of the samples were prepared by using the solid-state reaction method. Y_2O_3, $BaCO_3$, CuO, and other 3*d* oxides were mixed, pressed, and sintered in the appropriate proportions under identical conditions. The sintering process was carried out at 950 °C in an oxygen atmosphere with a few intermediate grindings. The parent sample $YBa_2Cu_3O_{6+y}$ was also made for comparison. The resistance of the samples was determined by using a standard four-wire probe with a computer controlled data-acquisition system. T_c was chosen to be the midpoint of the superconducting transition. Magnetic susceptibility was measured with a SQUID magnetometer in the temperature range 5–400 K. X-ray diffraction revealed that the samples were all single phased, with the same perovskite-type structure as in the 1-2-3 compound. Except for minor differences, the peak positions for both the substituted and pure copper 1-2-3 compounds coincided. This important fact allowed us to compare their superconducting properties. Detailed analysis of the diffraction patterns will be published elsewhere.

Figure 1 shows the temperature dependence of the normalized resistance for several samples. The parent composition has the highest T_c of 94.5 K and a very small transition width of about 1 K. Substitutions by 3*d* elements produce a reduction in T_c which is dependent on the substituting element. It is interesting to note that for A = Fe, Co, Ni, and Zn, the conduction electrons appear to become weakly localized before superconductivity sets in, as manifested by the increasing resistance at low *T*.

All samples which are superconducting (except A = Zn) showed the Meissner effect at low temperatures. In Fig. 2, magnetization and susceptibility data for the pure and Fe substituted 1-2-3 compounds as functions of tempera-

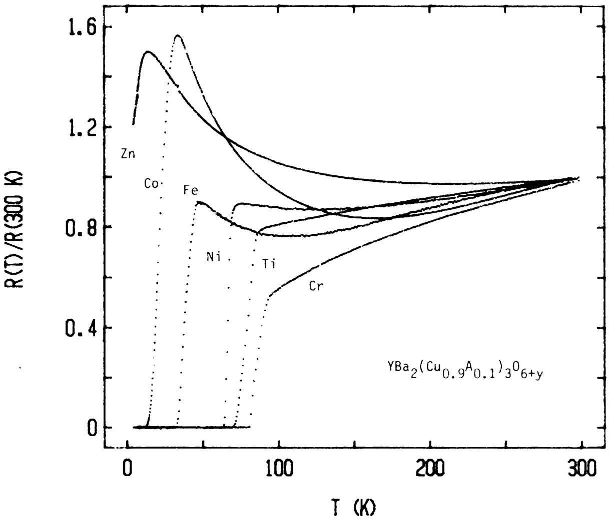

FIG. 1. Temperature dependence of the normalized resistance of $YBa_2(Cu_{0.9}A_{0.1})_3O_{6+y}$, where A = Cr, Mn, Fe, Co, Ni, and Zn.

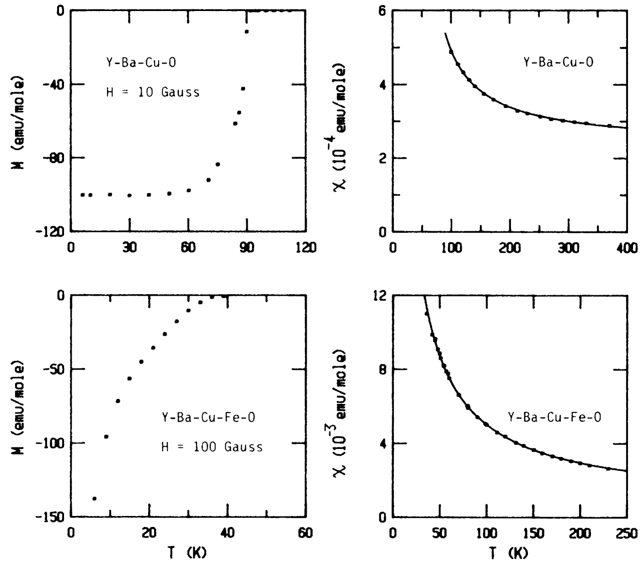

FIG. 2. Magnetization measurements below T_c (left) and temperature dependence of magnetic susceptibility above T_c (right) of $YBa_2Cu_3O_{6+y}$ and $YBa_2(Cu_{0.9}Fe_{0.2})_3O_{6+y}$. The solid curves are the best fit results to Eq. (1).

ture are presented. At $T=10$ K, the diamagnetic signal for the single phase 1-2-3 parent compound indicated that the superconductivity occurs in bulk form. Above T_c, the susceptibility becomes positive in every sample, and can be fitted very well by a Curie-Weiss law of the form

$$\chi=\chi_0+Np_{\mathrm{eff}}^2\mu_B^2/3k_B(T-T_0)\ . \tag{1}$$

Here χ_0 is temperature independent (resulting from diamagnetism and Pauli paramagnetism), N is the number of magnetic ions, p_{eff} is the effective magnetic moment in units of μ_B, and T_0 is the Curie-Weiss temperature. The values of T_c and susceptibility at $T=100$ K are plotted in Fig. 3 for the different $3d$ elements. The variation in T_c with substituting element is very systematic, but not monotonic. Early $3d$ elements affect T_c slightly; however, T_c suffers a dramatic reduction in 1-2-3 compound with mid-$3d$ element substitution (i.e., $A=$Fe, Co). T_c rises to a maximum in the pure copper compound. Examining the susceptibility data, there is a remarkable anticorrelation with T_c. As we will show later, the enhancement of susceptibility is due to the appearance of a large local paramagnetic moment in the mid-$3d$ elements. Therefore, we conclude that the T_c suppression arises from pair breaking by conduction and d-electron exchange scattering[4] at a paramagnetic site. This is to be contrasted with the rare-earth substitution results,[3] mentioned earlier, which show that the large localized moment of the rare-earth ions does not couple to the superconducting state. This indicates that not only is the coupling between the conduction of $4f$ electrons weak, but that the DOS(E_F) at the rare-earth sites must also be very low. At the Cu sites, the s-d exchange interaction is much stronger, and the relatively large conduction electron density at the Cu sites insures that the superconductivity will be sensitive to the presence of magnetic ions on those sites.

Besides the dip in the mid-$3d$ region, T_c drops precipitously as 10% of the Cu is replaced by Zn. This is a very dramatic effect which clearly cannot be caused by the local magnetic moment of the Zn ion, since the susceptibility of the Zn 1-2-3 compound is not much larger than that of the pure 1-2-3 material. Most likely, this is due to the filling of the electronic bands. Divalent Zn ions have ten $3d$ electrons, which is a very stable electronic structure. In the pure 1-2-3 compound, each Cu atom is octahedrally coordinated by oxygen ions. The divalent Cu ion has 9 electrons; therefore the DOS(E_F) comes mainly from the antibonding $d_{x^2-y^2}$ band, which is about half filled. Substitution of Cu by Zn provides an extra electron, which fills up the $d_{x^2-y^2}$ band and reduces the DOS(E_F) at those sites. The fact that T_c almost vanishes with the substitution of Zn at 10% of the Cu sites clearly demonstrates the importance of the antibonding $d_{x^2-y^2}$ orbitals for superconductivity in 1-2-3 compound.

From the susceptibility measurements of $YBa_2Cu_3O_{6+y}$ (Fig. 2), Cu ions carry a small paramagnetic moment of $0.22\mu_B$ with a small but positive Curie-Weiss temperature. The value of this moment is much smaller than the moment of free Cu^{2+} and Cu^{3+} (1.9 and $3.2\mu_B$, respectively). When $YBa_2Cu_3O_{6+y}$ is alloyed with a $3d$ element, both the Cu and A site may carry a magnetic moment. According to relation (1), the effective magnetic moment of Cu and A should satisfy the following approximated relation

$$0.1p_A^2+0.9p_{\mathrm{Cu}}^2=p_{\mathrm{eff}}^2\ , \tag{2}$$

where p_{eff} is the measured magnetic moment from the Curie-Weiss law, p_A and p_{Cu} are the respective moments of A and Cu, and 0.1 and 0.9 are the relative concentrations of the A and Cu ions. In order to determine p_A, we need to know p_{Cu}, which may vary from the value obtained from the parent composition. Fortunately, p_{Cu} is

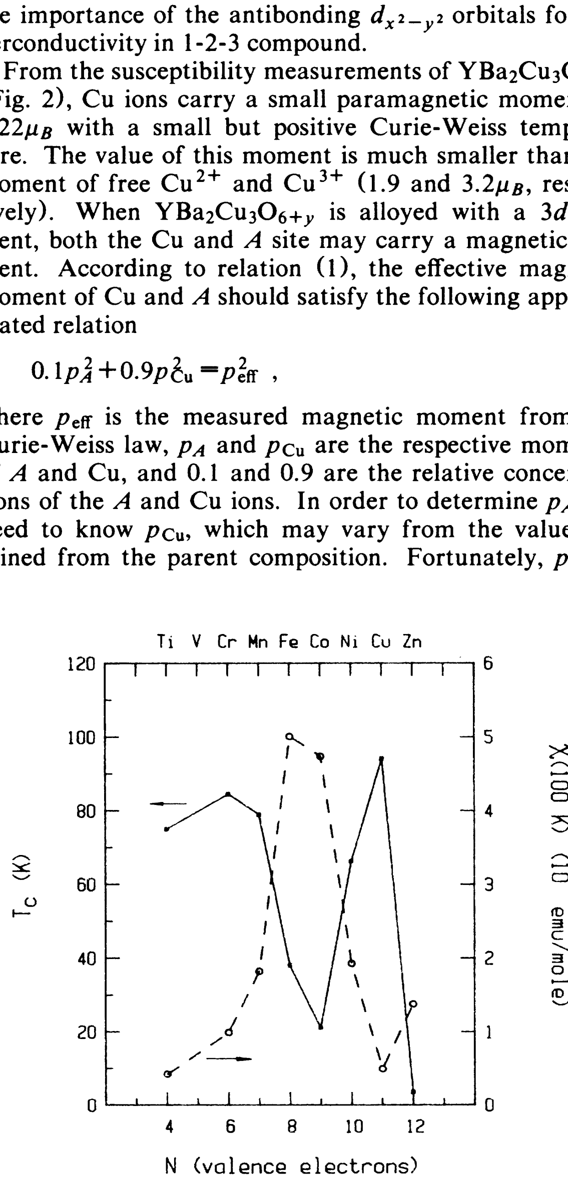

FIG. 3. T_c (solid line) and magnetic susceptibility at 100 K (dashed line) of $YBa_2(Cu_{0.9}A_{0.1})_3O_{6+y}$, where A is a $3d$ element, as a function of the number of valence electrons.

TABLE I. T_c; measured susceptibility at 100 K; fitted values of χ_0, C, and T_0; and the deduced values of p_A for $YBa_2(Cu_{0.9}A_{0.1})_3O_{6+y}$.

$A=$	T_c (K)	χ_{exp} (100 K) $\times 10^3$ emu/mol	χ_0^{fit} $\times 10^4$ emu/mol	C^{fit} emu K/mol	T_0^{fit} (K)	p_A
Ti	75.0	0.419	2.554	0.007	54.0	0–0.45
Cr	84.5	0.988		≈ 0		≈ 0
Mn	78.9	1.821	8.187	0.143	−39.3	1.35–2.01
Fe	38.0	5.004	7.405	0.458	−7.1	3.29–3.61
Co	21.2	4.735	8.786	0.369	3.3	2.87–3.20
Ni	66.3	1.923	2.395	0.148	9.6	1.40–2.05
Cu	94.1	0.490	2.362	0.017	33.9	0.22
Zn	< 3.0	1.378	1.268	0.083	30.5	0.49[a]

[a] This moment is assumed to reside on the copper sites, and was used as the upper limit of the Cu moment.

rather small compared to the p_{eff} of Mn, Fe, Co, and Ni. We can make an estimation of their moments by assuming that p_{Cu} lies between 0 and $0.5\mu_B$, which gives the ranges of p_{eff} for the Mn, Fe, Co, and Ni ions listed in Table I. As we can see, these ions all possess substantial magnetic moments, with the Fe and Co ions having the largest moments.

The suppression of T_c due to magnetic scattering in this class of materials is much smaller than in the transition-metal superconductors. Matthias[5] has shown that T_c is dramatically reduced when $Mo_{0.8}Re_{0.2}$ was doped with Cr, Fe, Co, and Ni. In the case of Fe, a few tenths of an atomic percent dragged the T_c from 10 K to below 1 K. It has also been observed that a few hundred *ppm* of Fe reduces the T_c of Mo from 0.9 K to below 0.3 K.[6,7] In the $YBa_2Cu_3O_{6+y}$ sample, even with Fe or Co substituting 10% of the Cu, T_c still has a sizable value, which shows the rather large coupling strength of the Cooper pairs.

In conclusion, we have observed a strong correlation between the superconducting transition temperature and the magnetic and electronic characteristics of the 3*d* element alloyed with the $YBa_2Cu_3O_{6+y}$ system. Formation of a localized moment in the mid-3*d* element region suppresses T_c, due to the effect of magnetic impurity scattering. At the end of the 3*d* series, Zn displays a phenomenal ability to suppress superconductivity, which is explained by the reduction of the density of states at the Fermi level as the *d* electrons in Zn fill up the $d_{x^2-y^2}$ antibonding band.

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