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The effect of doping with tantalum on the properties of $YBa_2Cu_3O_{7-y}$

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Abstract. $YBa_2Cu_{3-x}Ta_xO_{7-y}$ ($x = 0$, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) superconductors have been prepared. X-ray diffraction shows that the system remains orthorhombic for all compositions studied but, for $x > 0.2$, Ta_2O_5 was detected as an impurity phase. Substitution of Ta^{5+} for Cu^{2+} occurs in the Cu(2)–O planes. The introduction of the high-valence element tantalum produces extra free electrons. These electrons recombine with the positive carrier of the system, which causes the mobility and the Hall number of $YBa_2Cu_{3-x}Ta_xO_{7-y}$ to decrease and also results in a depression in T_c.

1. Introduction

Since the discovery of high-T_c superconductors [1], investigations of the basic properties in high-T_c superconductivity have been made theoretically and experimentally [2–4]. Now it is well established that the Cu(1)–O chains play an important role in stabilizing the crystal structure and coupling the Cu(2)–O planes. The Cu(2)–O planes are the key to the motion of superconducting electrons in $YBa_2Cu_3O_{7-y}$ [5]. It is noted that the carrier density $p = 1/eR_H$ is strongly correlated to T_c in $YBa_2Cu_3O_{7-y}$ [6]. With increasing p, T_c increases, reaches a maximum and then decreases as p increases further. In addition, $1/eR_H$ decreases linearly with temperature as does the resistivity for $T > T_c$. The carrier–phonon and the carrier–carrier scattering mechanisms have been assumed to explain the behaviour mentioned above. However, the effect of a high-valence ion dopant on the resistivity, the Hall coefficient and the Hall mobility have not been studied.

In this paper the resistivity and the Hall effect have been investigated on samples of $YBa_2Cu_3O_{7-y}$ doped with tantalum in order to observe the change in the carrier density due to the recombination of free electrons and holes, to examine the T_c versus p relation and to determine the mobility dependence of doping concentration. It is observed that the transition temperature, the Hall number and the Hall mobility decrease with increasing tantalum content. The change is attributed to the influence of the tantalum dopant on the Cu(2)–O planes.

2. Experimental details

Samples of $YBa_2Cu_{3-x}Ta_xO_{7-y}$ ($x = 0$, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) were prepared by conventional solid state reaction [7]. Analytical-reagent-grade Y_2O_3, $BaCO_3$, CuO and

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Ta_2O_5 were used as the starting materials. The mixed powders were thoroughly ground in a mortar and then placed in a corundum crucible, pre-heated at 920 °C for 30 h in air. Grinding and firing were repeated until complete homogeneity of the resulting materials was ensured. The black powders were reground and pressed into pellets of diameter 13 mm under a 25 MPa atmosphere. Finally, the pellets were sintered at 930 °C for 30 h in air. The x-ray diffraction patterns were recorded with a Rigaku Denki 2028 D/max-IIB diffractometer using Cu Kα ($\lambda = 0.1542$ nm) radiation. Silicon powder was used as the internal standard. The thermal analysis was carried out by means of a Beijing Prt-I thermobalance at a rate of 10 °C min^{-1} under argon flowing at 500 ml min^{-1}. The DC Hall coefficient and DC resistivity were measured by the Van der Pauw method, and electrical contacts were made with the standard pressed-In four-interval method. The AC magnetic susceptibility was measured by the mutual inductance method.

3. Results and discussion

The crystal data show that the $YBa_2Cu_{3-x}Ta_xO_{7-y}$ samples remain orthorhombic for all the samples reported in this paper. Also a Ta_2O_5 impurity phase and a few unidentified weak peaks appear in the x-ray diffraction pattern for $x > 0.2$. The intensity of the Ta_2O_5 peaks gradually increases with increasing x. Their lattice parameters were calculated and are given in table 1.

Table 1. Lattice parameters for $YBa_2Cu_{3-x}Ta_xO_{7-y}$. The systematic errors are ±0.05%.

x	a (Å)	b (Å)	c (Å)	V (Å^3)
0.0	3.8206	3.8850	11.666	173.16
0.1	3.8282	3.8979	11.7069	174.69
0.2	3.8282	3.8989	11.7140	174.84
0.3	3.8282	3.9001	11.7171	174.94
0.4	3.8286	3.9064	11.7176	175.24
0.5	3.8282	3.9076	11.7180	175.29
0.6	3.8279	3.8993	11.7084	174.76

As shown in table 1, there are systematic increases in the parameters b and c and a slight increase in the parameter a. This suggests that some of the Ta ions may enter the $YBa_2Cu_3O_{7-y}$ lattice and others are in the Ta_2O_5 impurity phase coexisting with the system.

Generally, one oxygen atom per formula unit of $YBa_2Cu_3O_{7-y}$ can be removed within the undoped phase by heating in argon. Since this oxygen is removed only from the Cu(1)–O chains, it is expected to be strongly affected by the replacement of the high-valence Ta ions for the Cu(1) ions because of changes in the strength of the M–O bonds, but weakly affected by substitution within the Cu(2)–O planes. Thus TGA measurements should be a powerful tool for determining whether the substitution is taking place on Cu(1) or Cu(2) sites [8]. Therefore, we performed TGA measurements on $YBa_2Cu_{3-x}Ta_xO_{7-y}$ samples and the results are given in figure 1.

The results for $YBa_2Cu_{3-x}Co_xO_{7-y}$ are given in figure 1 for comparison. As shown, the amount of oxygen removed from the compound decreases monotonically with increasing Co concentration. However, the amount of removable oxygen is nearly independent of tantalum concentration according to the TGA curves. This suggests that the substitution of Co for

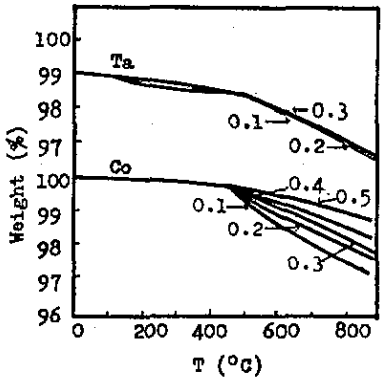

Figure 1. TGA curves for $YBa_2Cu_{3-x}Ta_xO_{7-y}$.

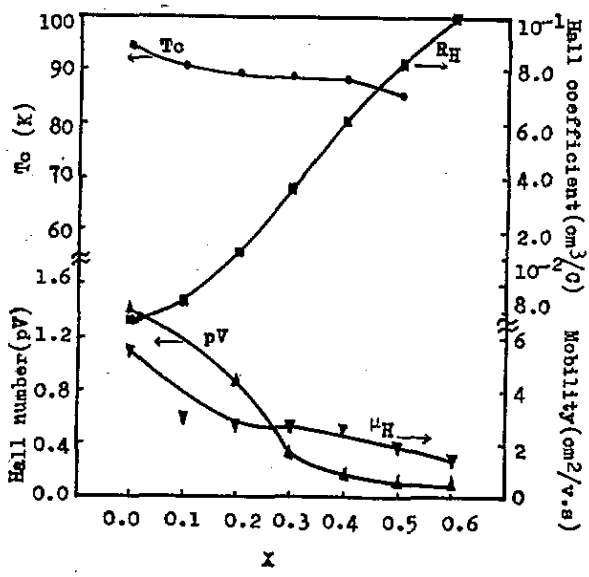

Figure 2. Dependence of the Hall parameters on x for $YBa_2Cu_{3-x}Ta_xO_{7-y}$: ●, T_c; ■, R_H; ▲, pV; ▼, μ_H.

Cu occurs on the Cu(1) sites in Cu(1)–O chains [8]. Therefore, the difference between the TGA curves for Co- and Ta-doped samples might indicate that the replacement of tantalum for copper is preferentially taking place on the Cu(2) sites on the Cu(2)–O planes. This substitution, indeed, has a weaker effect on the crystal structure but a stronger effect on the electrical behaviour of $YBa_2Cu_{3-x}Ta_xO_{7-y}$.

Figure 2 shows the dependences of the Hall number, defined as the charge carrier density per unit cell ($pV = V/R_He$), and the mobility on tantalum concentration.

In figure 2, the measured value of T_c decreases linearly with increasing tantalum concentration. The same trend is also shown in the variation in the Hall number with increasing x. On the other hand, the carrier mobility also monotonically decreases whereas the Hall coefficient progressively increases with increasing tantalum concentration.

Generally, the Hall effect reflects the dynamics of electronic transport. The Hall effect is explained by collision-dominated transport or electron scattering in the low-field region. An applied field B of 10 kG was used in our experiments and the condition $B \ll 1$ was fulfilled, which means that the Hall voltage is measured in the low-field region. To explain the change in the Hall coefficient, we consider two kinds of carrier system. Thus R_H can generally be written as [9]

$$R_H = R_1[\sigma_1/(\sigma_1+\sigma_2)]^2 + R_2[\sigma_2/(\sigma_1+\sigma_2)]^2 = (1/e)(p-nb^2)/((p+nb)^2)$$

where $b = \mu_e/\mu_h$, n is the electron density and p is the hole density.

Duan *et al* [10] showed that the temperature dependence of R_H was the result of coupling between Cu(2)–O planes in $YBa_2Cu_3O_{7-y}$. So, the Cu(2)–O planes play an important role in the motion of superconducting electrons. Since there is a difference between the valence states of tantalum and copper, the tantalum ions can provide extra free electrons for the system. These free electrons compensate the holes, resulting in recombination between

the free electrons and holes. This makes the carrier concentration, i.e. the hole density, decrease with increasing dopant. Replacement of Cu^{2+} by Ta^{5+} relaxed the repulsive interaction between Cu(2)–O(2) or Cu(2)–O(3) bonds in Cu(2)–O planes. This should lead to a reduction in the interaction between Cu^{2+} $d_{x^2-y^2}$ and O^{2-} p_σ and a depression in the splitting energy between the $d_{x^2-y^2}$ and d_{z^2} orbitals. Simultaneously, the decrease in the carrier mobility with increasing tantalum concentration indicates that the substitution of Ta^{5+} for Cu^{2+} does affect the motion of superconducting electrons. It is different from the result of substitution of Co for Cu on Cu(1)–O chains in $YBa_2Cu_3O_{7-y}$. In that case the carrier mobility has not obviously changed although the carrier density has a faster depression [11]. Because the Hall number decreases, the critical transport temperature is also reduced for $YBa_2Cu_{3-x}Ta_xO_{7-y}$.

Acknowledgments

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