

# Superconductivity in $(\text{Bi,Pb})_2\text{Ca}_2\text{Sr}_2\text{Cu}_{3-x}\text{V}_x\text{O}_y$

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The superconducting properties of V-doped  $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  (2223) samples have been investigated by means of X-ray diffraction and electrical resistivity measurements. The volume fraction of the 2223 phase decreases with a decrease in the  $c$  lattice parameter. The onset of superconductivity in the samples remains almost constant while the temperature at which the resistivity becomes zero decreases with increasing dopant content. The electrical resistivity data suggest that the substitution of copper by vanadium suppresses the superconductivity in  $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_{3-x}\text{V}_x\text{O}_y$  by destroying the phase coherence and by pair-breaking effects. The suppression of superconductivity in the system could also be due to a decrease in the carrier concentration.

## 1. Introduction

One of the currently interesting areas of superconductivity research that is receiving a great deal of attention is substitutional studies. Substitution acts as a probe of the chemical and structural environment which determines whether or not the system exhibits superconductivity.

In the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  superconductor, the replacement of yttrium by other rare-earth elements, even those that possess a high magnetic moment, does not have any significant effect on the critical temperature and has led to the belief that the superconductivity is associated with the  $\text{Cu}(2)\text{-O}$  layers and  $\text{Cu}(1)\text{-O}$  chains. On the other hand, it has been shown that atoms which are able to replace the Cu atoms on the  $\text{Cu-O}$  chains or  $\text{Cu-O}$  layers have a definite influence on the critical temperature [1–5].

Since superconductivity in the Bi-based systems is believed to be associated with the  $\text{Cu-O}_2$  planes, most of the substitutional studies have been made at the Cu site [6, 7]. A consideration of the relative valences and radii suggests that the 3d transition metals seem to be the most attractive elements to substitute for Cu in these materials. All doping elements so far investigated lower the transition temperature.

The mechanisms proposed as being responsible for the decrease and eventual suppression of the transition temperature in the copper oxide based superconducting systems are magnetic pair breaking, a change in the oxygen vacancy positions and local symmetry and electronic mechanisms such as band filling and electronic localization [1–8].

In this work, the effect of the substitution of V for Cu in the  $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  (2223) system is investigated. Lönnberg *et al.* [6] have shown that the substitution of V for Cu in the 2212 (80 K) phase of the Bi-based systems results in a decrease in the critical temperature. Nkum *et al.* [7] have investigated the effect of the substitution of Cu by Mn, Fe, and Zn on the superconducting properties of the 2223 (110 K)

phase of the system. Pair-breaking effects created by the doping were invoked to provide a satisfactory explanation of the reduction of the critical temperature of the studied samples.

In this work, the superconducting properties of the  $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_{3-x}\text{V}_x\text{O}_y$  system have been studied and a possible mechanism for the reduction of the critical temperature is presented.

## 2. Experimental procedures

The V-doped samples were prepared from  $\text{Bi}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{CuO}$  and  $\text{V}_2\text{O}_3$  powders (each 99.99% pure) in the correct stoichiometric amounts to produce samples with compositions of  $\text{Bi}_{1.84}\text{Pb}_{0.34}\text{Sr}_{1.91}\text{Ca}_{2.03}(\text{Cu}_{1-x}\text{V}_x)_{3.06}\text{O}_y$  ( $0 \leq x \leq 0.1$ ). The powders were then pressed into pellets of 9 mm diameter and 1 mm thickness under a pressure of  $4 \times 10^8$  Pa. The pellets were then calcined at  $820^\circ\text{C}$  for 6 h. The resulting materials were crushed, ground, pressed into pellets and sintered at  $852^\circ\text{C}$  for a further 100 h with several intermediate grindings and pressings. At the end of the heat treatment the pellets were cooled to  $750^\circ\text{C}$  at the rate of  $0.1^\circ\text{C min}^{-1}$  and then to room temperature at  $0.2^\circ\text{C min}^{-1}$ .

The crystalline phases in the samples were studied by X-ray powder diffraction. All the diffraction patterns were recorded with a Nicolet diffractometer using  $\text{CuK}_\alpha$  radiation and a step-scanning device able to count and record angular steps of  $0.01^\circ$  ( $2\theta$ ). The critical temperature was determined from electrical resistivity measurements. The standard four-probe technique was used for the electrical resistivity measurements.

## 3. Results and discussion

The X-ray diffraction patterns of the samples indicate that the undoped sample ( $x = 0$ ) solely has peaks that belong to the 2223 structure. A few peaks that belong

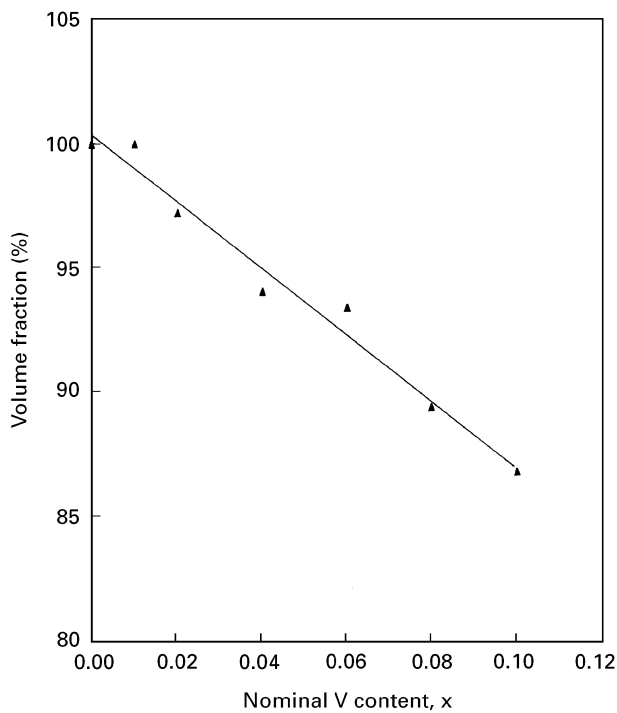


Figure 1 The dependence of the volume fraction of the 2223 phase on the nominal dopant content.

to the 2212 phase appear in the pattern of the  $x = 0.02$  sample; the intensities of these peaks increase with increasing dopant concentration,  $x$ . This shows that the volume fraction of the 2223 superconducting phase decreases with  $x$  while the amount of the 2212 superconducting phase increases. This point is highlighted in Fig. 1 which shows the dependence of the volume fraction of the 2223 superconducting phase on the vanadium concentration. The volume fraction was determined by comparing the peak intensity of the  $(00\bar{1}0)$  peak for the 2223 phase with the intensity of the neighbouring  $(008)$  peak of the 2212 phase. No impurity phases were observed in the diffraction patterns. It is possible that the intensities of peaks belonging to any impurity phase present were too weak to be detected.

The samples all possessed an orthorhombic structure. It was observed that no significant changes occurred in the  $a$  and  $b$  lattice parameters. The average values for the  $a$  and  $b$  parameters are 0.53908 nm and 0.54134 nm, respectively. The variation of the  $c$ -lattice parameter as a function of the nominal dopant concentration is shown in Fig. 2. The  $c$  parameter is seen to decrease monotonically with the vanadium concentration. Whereas the 2212 and 2223 phases of the Bi-based superconducting systems have almost the same values for the  $a$  and  $b$  lattice parameters, the  $c$  lattice parameters are about 3.07 and 3.71 nm, respectively. Thus, the superconductivity in the Bi-based systems depends on the  $c$  lattice parameter. Fig. 3 shows that the volume fraction of the 2223 phase of the vanadium doped system decreases as the  $c$  lattice parameter decreases.

The temperature dependence of the electrical resistivity of samples that contain the 2223 phase along with the undoped sample that have an onset temperature,  $T_c^{\text{on}}$ , of 110.5 K are shown in Fig. 4. The

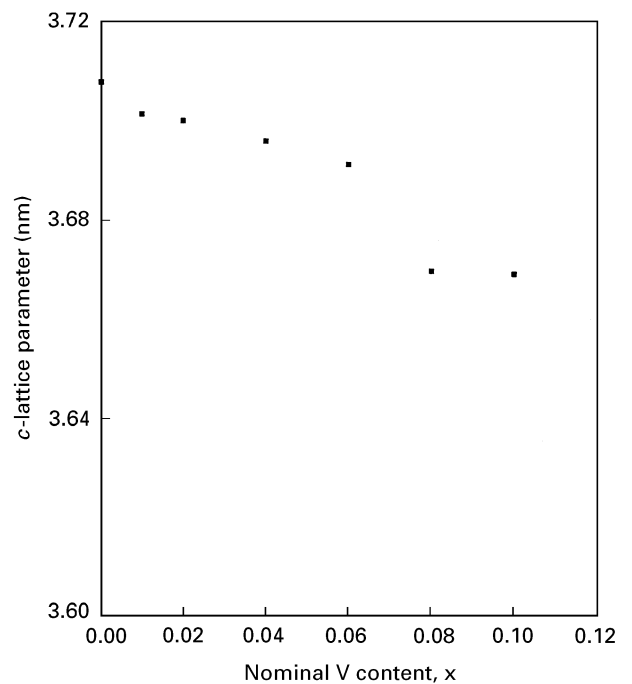


Figure 2 Variation of the  $c$ -lattice parameter with the nominal dopant content.

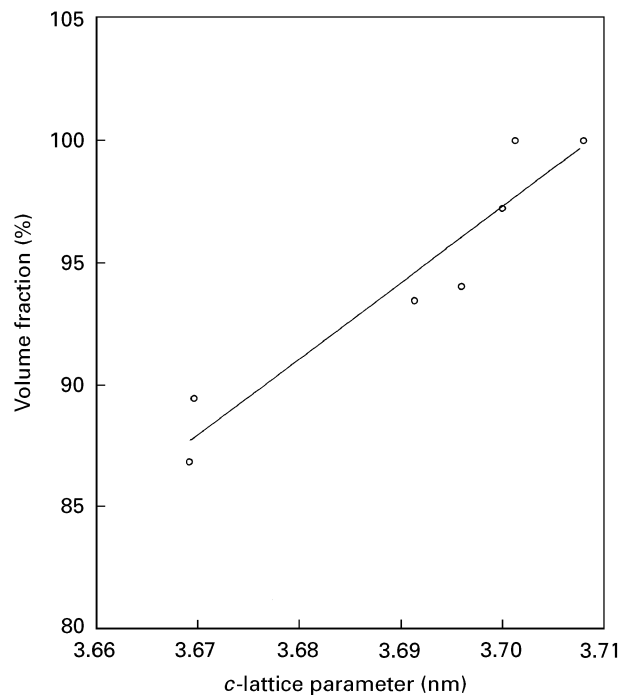


Figure 3 Dependence of the volume fraction of the 2223 phase on the  $c$ -lattice parameter.

temperature of the onset of the superconducting transition is determined as demonstrated in Fig. 5.

It is seen from the data of Fig. 4 that the onset of superconductivity is almost constant for the samples while the temperature at which the resistivity becomes zero ( $T_c^{\rho=0}$ ) decreases with increasing vanadium concentration. For a pair wavefunction  $\psi = \psi_0 e^{-i\phi}$ , superconductivity may be destroyed by reducing the amplitude ( $\psi_0$ ) or by destroying the phase coherence ( $\phi$ ). The two modes manifest themselves differently. In the case of amplitude reduction, the temperature of

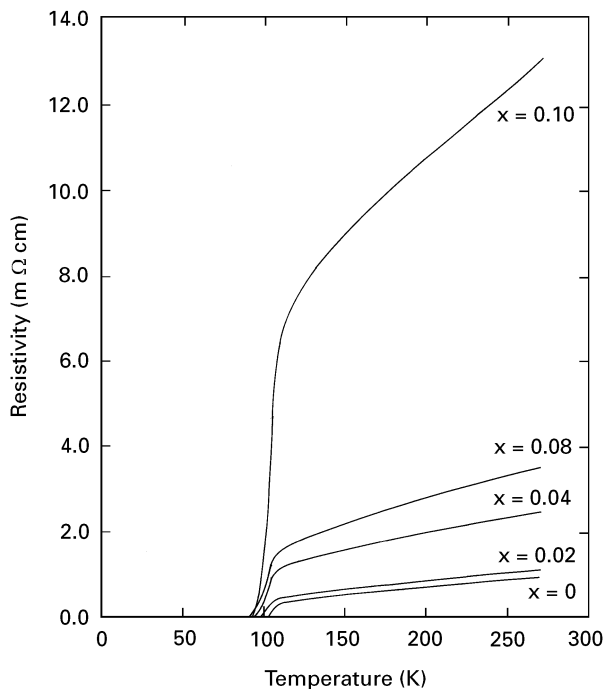


Figure 4 Temperature dependence of the electrical resistivity of  $(\text{Bi, Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_{3-x}\text{V}_x\text{O}_y$ .

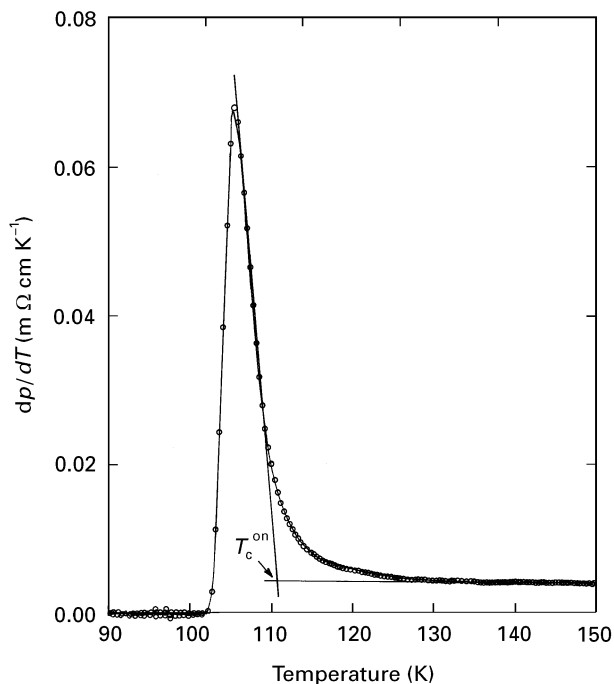


Figure 5 Temperature dependence of  $dp/dT$ . The  $T_c^{\text{on}}$  marked in the figure is the onset of superconductivity.

the onset of superconductivity remains well defined and decreases [9, 10]. In the case of phase breaking, the onset of superconductivity remains unchanged, but the current-carrying capacity disappears [11, 12]. This means that the temperature at which the resistivity becomes zero decreases and the transition width increases until the material has no region of zero resistivity. The data of Fig. 4, therefore, suggests that the substitution of vanadium suppresses superconductivity in  $(\text{Bi, Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_{3-x}\text{V}_x\text{O}_y$  by destroying the phase coherence.

The suppression of the superconductivity in the samples under investigation could also be due to pair-breaking effects. The pairing of the carriers in the  $\text{Cu-O}_2$  planes is responsible for the superconductivity in the Bi-based systems. A replacement of some of the copper atoms with other types of atoms will, therefore, change the superconducting properties and alter the electronic structure. Doping will thus provide information on the pairing mechanism. The exchange interaction between the electrons and the spinning impurity atoms leads to nonconservation of the electron spin, which may affect the formation of Cooper pairs. It is possible that the spin of the dopant prevents the appearance of the superconducting correlation and thus causes a decrease in  $T_c^{\rho=0}$ .

The pair-breaking theory of Abrikosov and Gor'kov [13] for low values of paramagnetic impurity concentration,  $x$ , results in the following expression:

$$T_c \simeq T_{c0} - [(\pi^2/4k_B)N(E_F)\mathbb{J}^2(g-1)^2J(J+1)]x \quad (1)$$

where  $T_{c0}$  is the value of  $T_c$  in the absence of a magnetic field,  $N(E_F)$  is the density of states at the Fermi level,  $g$  is the Landé factor,  $J$  is the total angular momentum of the ground state of the magnetic ion, obtained using Hund's rules and  $\mathbb{J}$  is the exchange-interaction parameter. Equation 1 predicts a suppression of  $T_c$  with paramagnetic impurity concentration  $x$  that is linear in the low-concentration region. There are two material parameters,  $N(E_F)\mathbb{J}^2$  and the de Gennes factor  $(g-1)^2J(J+1)$  in Equation 1 which determine the  $T_c$  versus  $x$  dependence.  $N(E_F)\mathbb{J}^2$  characterizes the hybridization between conduction electron states and local impurity states and their spin-dependent exchange interaction. The de Gennes factor is a characteristic of the magnetic moment of the impurity ion.

The  $T_c^{\rho=0}$  versus  $x$  data shown in Fig. 6 indicate that the temperature at which the resistivity goes to zero decreases monotonically with increasing dopant concentration in the region  $(0 \leq x \leq 0.1)$  considered. This result can be interpreted as evidence for the magnetic pair-breaking effects by V. Data for Zn and Fe from Nkum *et al.* [7] are included in Fig. 6 for comparison. It can be seen that the suppression rate,  $dT_c^{\rho=0}/dx$ , for V is different from those of Zn and Fe in that Zn and Fe are found to be more effective in suppressing the superconductivity in the Bi-based systems than V. As pointed out in an earlier work [7], pair breaking effects in the superconducting oxides are not restricted to magnetic scattering but could also be due to scattering by nonmagnetic disorder or changes in the spin fluctuations. At small dopant concentrations, both Zn and Fe depress the  $T_c^{\rho=0}$  at approximately the same rate.

In addition to the spin of V preventing the appearance of superconducting correlations and thus causing a decrease in the transition temperature, V-doping could also reduce the number of free carriers in the system. Evidence of this can be obtained from the slope of the resistivity-temperature curve,  $dp/dT$ , in the normal state. It can be observed from Fig. 4 that,  $dp/dT$  increases with  $x$  and according to the free electron model,  $dp/dT$  is inversely proportional to the

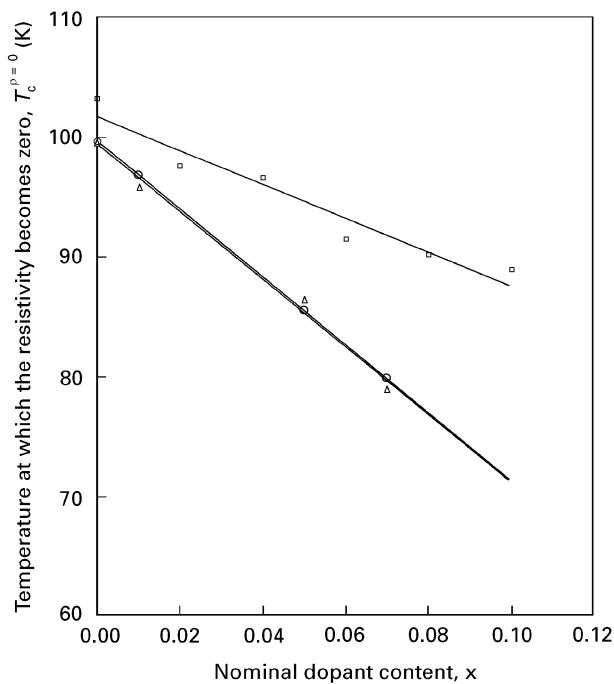


Figure 6 Nominal dopant concentration dependence of the temperature at which the resistivity becomes zero,  $T_c^{\rho=0}$ : ( $\square$ ) V, (this work) ( $\circ$ ) Zn, and ( $\triangle$ ) Fe (reference [7]).

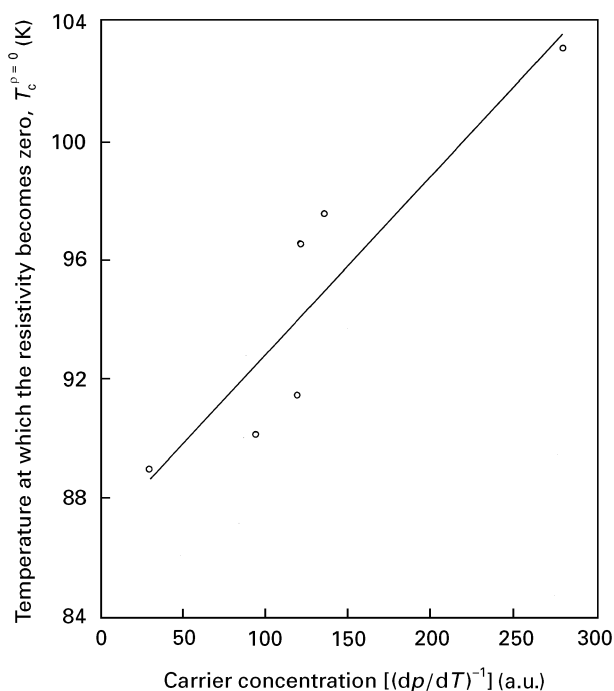


Figure 7 The dependence of the temperature at which the resistivity becomes zero,  $T_c^{\rho=0}$ , on the carrier concentration. The straight line is to act as a guide to the eye.

carrier concentration [14]. Thus, in the samples studied, the carrier concentration decreases with increasing dopant concentration. This decrease in the carrier concentration results in the suppression of superconductivity and hence a decrease in  $T_c^{\rho=0}$ . This is demonstrated in Fig. 7 which indicates that  $T_c^{\rho=0}$  decreases monotonically as the carrier concentration decreases. It must be noted that  $dp/dT$  is

determined at higher temperatures, where the resistivity-temperature curve is linear.

#### 4. Conclusion

In summary, the superconducting properties of the V-doped 2223 system have been investigated. The volume fraction of the 2223 phase, determined from X-ray diffraction patterns, decreases with increasing dopant concentration. The  $c$  lattice parameter is also found to decrease with the increase in dopant concentration. Thus, the volume fraction of the 2223 phase depends on the  $c$  lattice parameter. From the electrical resistivity data, the onset temperature for superconductivity is almost constant for all the samples while the temperature at which the resistivity becomes zero decreases with increasing dopant concentration. This provides evidence for the hypothesis that superconductivity in the V-doped samples is suppressed by the destruction of the phase coherence. The  $T_c^{\rho=0}$  versus V concentration,  $x$ , plot shows a linear relation. This result provides evidence for the pair-breaking effects of V. The carrier concentration decreases with increasing dopant concentration leading to the suppression of superconductivity.

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