Magnetism and superconductivity in 3d-metal-substituted Bi-based cuprates having the 2:2:0:1 structure

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The effects of the substitution for Cu or Mn by either a magnetic (Ni) or a nonmagnetic (Zn) 3d metal on the physical properties of the superconducting compounds $\text{Bi}_{1.2}\text{Pb}_{0.8}\text{La}_{0.5}\text{Sr}_{1.5}\text{CuO}_{6+y}$ and of the antiferromagnetic insulating phases $\text{Bi}_2\text{Sr}_2\text{MnO}_{6+y}$ and $\text{BiPbSr}_2\text{MnO}_6$, all isostructural to the 10-K superconducting $\text{Bi}_2\text{Sr}_2\text{CuO}_z$ (2:2:0:1) phase, have been investigated with use of x-ray powder diffraction, susceptibility, and resistivity measurements. We found that both Ni and Zn substitute for Cu and Mn with a range of solubility strongly dependent upon the nature of both the dopant and the host compound. For instance, in the Cu-based compounds the range of solubility is only a few percent (5% for Ni and 2% for Zn) whereas in the Mn-based compounds the range of solubility can be extended up to 20% for Zn or 30% for Ni. In the superconducting $\text{Bi}_{1.2}\text{Pb}_{0.8}\text{La}_{0.5}\text{Sr}_{1.5}\text{Cu}_{1-x}\text{M}_x\text{O}_{6+y}$ system, both Ni and Zn depress the T_c at approximately the same rate (8 K/mol %), so that the magnetism of the dopant has no effect on the T_c as observed for the other high- T_c cuprates. The Mn-based materials order antiferromagnetically and we found that upon substitution by Ni and Zn the antiferromagnetic transition temperature T_N decreases less dramatically for the magnetic Ni [5 K/(10 at. %)] than for the nonmagnetic Zn [30 K/(10 at. %)]. A consideration of the exchange interactions can account for these results.

INTRODUCTION

In the studies of high- T_c oxides, doping experiments have established general phenomenological trends that have enhanced the basic understanding of their physical properties.^{1,2} Excessive cationic and anionic substitutions have been carried out in the La-based (La_2CuO_4) (Refs. 3–6) and Y-based ($\text{YBa}_2\text{Cu}_3\text{O}_4$) (Refs. 7–10) compounds as well as for the Nd-Ce-Cu-O system.^{11,12} In contrast, only limited substitutional data are available for the Bi-based layered compounds.^{13,14}

For the La- and Y-based compounds solid solutions on the Cu site exist over a broad range of composition for various 3d metals (Ni, Zn, Fe, Co, ...). In contrast, in the Bi-based compounds of general formula $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_z$ the substitution for Cu by divalent ions Ni or Zn is limited to a few atomic percent (<2%), whereas the substitution by trivalent ions (Fe, Co, and Mn) can be complete.^{15–17} However, a main difference between the Bi-based compounds and the other cuprates is the presence of a structural modulation that originates in the Bi-O layers and that is associated with extra oxygens inserted in these layers. To determine whether this structural difference is the origin of the limited Ni or Zn substitution in these phases we decided to investigate the substitution for Cu or Mn by Ni and Zn in both modulated ($\text{Bi}_2\text{Sr}_{1.5}\text{La}_{0.5}\text{CuO}_z$ and $\text{Bi}_2\text{Sr}_2\text{MnO}_z$) and nonmodulated ($\text{Bi}_{1.2}\text{Pb}_{0.8}\text{Sr}_{1.5}\text{La}_{0.5}\text{CuO}_6$ and $\text{BiPbSr}_2\text{MnO}_6$) host materials [note that to obtain modulation-free material of the Cu-based compound the substitution of Bi by Pb

must be accompanied by a partial substitution of Sr by La (Ref. 20)].

For all high- T_c oxides it was found that substitution on the Cu site strongly depresses the T_c . Contrary to the well-established experimental and theoretical fact that within the low-temperature superconductors the presence of magnetic impurities depresses the T_c much stronger than that of nonmagnetic impurities,¹⁸ it was found that for La-based and Y-based compounds the magnetism of the dopant has no effect on the T_c . This behavior is associated with a much shorter correlation length in these materials (10–30 Å). When compared to the BCS-type materials (>300 Å), this leads to the conclusion that local disorder rather than magnetism is the important factor for the suppression of superconductivity in these materials. It has been shown, that the Nd-Ce-Cu-O compound, possessing a correlation length slightly larger (90 Å) than the other high- T_c cuprates, exhibits a behavior close to an ideal BCS system with respect to magnetic impurities.¹⁹ The T_c 's of the La-Sr-Cu-O and Nd-Ce-Cu-O systems are quite different (25 K for the Nd-based system instead of 40 K for the La-based system). A more convincing comparison will require a material with a similar T_c . The superconducting $n=1$ Bi-based phase whose T_c can be increased to 25 K (similar to the Nd-based system) upon doping provides a unique opportunity to reexamine the doping effect on two materials with nearly identical T_c 's. Thus, we decided to investigate the superconducting behavior of the Bi-layered compounds upon Ni and Zn substitution. We found that although the host Bi-

based layer material has the same T_c as the Nd-based system, its behavior with respect to Ni and Zn substitution resembles that of the high- T_c oxides and not of the Nd-based system.

Like the superconducting properties, the magnetism of the cuprates has been studied for possible links to superconductivity. Many of the high- T_c cuprates that have been found have related compounds that are antiferromagnetic insulators. For instance, replacing Cu by Mn in the 2:2:0:1 phase leads to the antiferromagnetic insulator $\text{Bi}_2\text{Sr}_2\text{MnO}_y$ that orders at $T_N = 150 \text{ K}$.^{17,22} Similarly for the superconducting properties, one would expect the magnetic properties of the antiferromagnetic insulating phases to be affected by any structural distortions, as well as by any modification of the magnetically active 3d-metal MO_2 layer. Thus, we studied how the substitution for Mn by Ni and Zn affects the T_N in the parent compound $\text{Bi}_2\text{Sr}_2\text{MnO}_y$, hoping that by studying the magnetism in these related compounds one will gain a better understanding of the cuprates.

EXPERIMENTAL

For different series of samples,

and

denoted *A*, *B*, *C*, and *D*, respectively, with $M = \text{Ni, Zn}$ and x ranging from 0 to 1, have been prepared by mixing stoichiometric amounts of the corresponding oxides or carbonates (Bi_2O_3 , PbO , SrCO_3 , La_2O_3 , CuO , MnO_2 , ZnO , and NiO) all 99.999% pure.

Samples of the series *A* and *B* were calcined at 800°C in air for 24 h, then reground in an agate mortar, heated up to 900°C , and held there for 24 h. To achieve better homogeneity, this step was repeated several times with the samples being pressed to pellets and reground between each step. The resulting samples were annealed under a stream of flowing oxygen for 48 h and quenched in air to room temperature. For the *B* series only, a part of each sample was additionally annealed at 900°C under flowing O_2 for three more days and quenched in liquid nitrogen.

The *C* and *D* series were prepared similarly as *A* and *B* but with a reducing ambient (N_2) instead of an oxidizing ambient (O_2). (The Bi-based manganese phases are not stable under an oxygen ambient for temperatures greater than 600°C .) The samples were heated up slowly (40 h) up to 970°C , held there for 48 h, and cooled slowly. To improve the homogeneity of the samples, this step was repeated several times again but the heating period was shortened to 3 h on subsequent heatings.

X-ray powder diffraction (using a SCINTAG-PADV diffractometer with $\text{Cu } K\alpha$ radiation) was performed for the characterization of all samples. Lattice parameters were calculated from x-ray-diffraction data using a least-

squares method. The solubility ranges determined by x rays reported below are defined by the dopant composition x of the first sample that shows weak extra Bragg peaks in the diffraction patterns. The presence of weak extra peaks associated with the structural modulation has made the determination of the solubility range in some samples less accurate. To monitor possible changes in the oxygen content TGA (thermogravimetric analysis) measurements in a reducing atmosphere (5% H_2 in Ar) were carried out for several samples by monitoring the weight loss of the material when heated on a sapphire substrate at a rate of $10^\circ\text{C}/\text{min}$ from 50 to 900°C .

The superconducting properties were determined using both standard four-probe resistivity and ac-susceptibility measurement techniques. Meissner fractions as well as the magnetic properties of the antiferromagnetic samples [series (*C*) and (*D*)], were measured with a superconducting quantum interference device (SQUID) magnetometer (SHE-Corp).

RESULTS

A. Cu-based compounds

The x-ray diffraction patterns of the Ni- and Zn-doped $\text{Bi}_2\text{La}_{0.5}\text{Sr}_{1.5}\text{Cu}_{1-x}\text{M}_x\text{O}_y$ samples with $x < 0.075$ were fully indexed on the basis of the orthorhombic unit cell reported in the literature. The very few weak extra lines remaining in the powder-diffraction spectra were related to the presence of an incommensurate modulation along the *a* axis in this compound. The occurrence of impurity lines in the x-ray-diffraction patterns of $\text{Bi}_2\text{La}_{0.5}\text{Sr}_{1.5}\text{Cu}_{1-x}\text{M}_x\text{O}_{6+y}$ ($M = \text{Ni, Zn}$) for samples with $x > 0.075$ suggests that the range of solubility is less than 10% for both elements.

Figure 1(a) shows the variation of the lattice parameters for the Ni- and Zn-doped $\text{Bi}_2\text{La}_{0.5}\text{Sr}_{1.5}\text{Cu}_{1-x}\text{M}_x\text{O}_y$ series. An increase in the lattice parameter *a* and *b* with increasing x for both Ni- and Zn-doped samples and a slight decrease in the lattice parameter *c* can be observed. Because of the small difference between the ionic radii of the dopant with respect to the substituent (the ionic radius of $\text{Ni}^{2+} = 0.69 \text{ \AA}$ and the ionic radius of $\text{Zn}^{2+} = 0.74 \text{ \AA}$ versus $0.73 \text{ \AA}$ for the ionic radius of Cu^{2+}) these changes in lattice parameters are somewhat surprising. This behavior may result from a different distortion of the transition-metal-oxygen octahedra due to the different Jahn-Teller effect of the 3d metals. Zn^{2+} , a d^{10} ion, has no Jahn-Teller effect in contrast to a d^9 ion such as Cu^{2+} . A Jahn-Teller distortion causes an elongation along the *c* axis of the oxygen octahedron surrounding the 3d metal, resulting in an increase of the *c/a* ratio. Thus as Cu^{2+} ions are replaced by Zn^{2+} ions one would expect the Jahn-Teller distortion to be reduced, leading to a decrease of the *c/a* ratio as observed experimentally [increase of $(a+b)/2$ and slight decrease in the lattice parameter *c*]. Like Zn^{2+} , Ni^{2+} should affect the structure in a similar way, consistent with the same trends in the lattice-parameter changes observed for both Ni- and Zn-doped samples.

However, changes of the unit-cell volume can also be related to changes in the oxygen content accompanying

FIG. 1. Unit-cell parameters (a , b , c , and V) as a function of dopant content x in (a) $\text{Bi}_2\text{La}_{0.5}\text{Sr}_{1.5}\text{Cu}_{1-x}\text{M}_x\text{O}_{6+y}$ and (b) $\text{Bi}_{1.2}\text{Pb}_{0.8}\text{La}_{0.5}\text{Sr}_{1.5}\text{Cu}_{1-x}\text{M}_x\text{O}_6$ for $M = \text{Ni}$ (triangles) and $M = \text{Zn}$ (circles).

the Zn and Ni substitutions. To test this possibility TGA measurements in an reducing atmosphere (5% H in Ar) were performed. No noticeable difference in weight loss could be detected within the limit of resolution of the method (better than 0.05 oxygen per formula unit). Thus, we rule out that the observed changes in the lattice constants can be related to a change in the oxygen content.

We now present the crystallographic data for the Ni- and Zn-doped $\text{Bi}_{1.2}\text{Pb}_{0.8}\text{La}_{0.5}\text{Sr}_{1.5}\text{Cu}_{1-x}\text{M}_x\text{O}_6$ systems (series B) in which Bi has been partially replaced by Pb. In this series it is much easier to determine the exact limit of solubility, since these materials do not show a structural modulation. Furthermore, the influence of substitution on the superconducting properties can also be used to determine this limit, as we will show later.

X-ray-diffraction patterns of the $\text{Bi}_{1.2}\text{Pb}_{0.8}\text{La}_{0.5}\text{Sr}_{1.5}\text{Cu}_{1-x}\text{M}_x\text{O}_6$ series could also be fully indexed based on the orthorhombic distorted subcell of $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+y}$, with a difference—that no modulation occurs in these compounds as shown by TEM (transmission electron microscopy) studies.²⁰ Figure 1(b) shows the variation of the orthorhombic lattice parameters. Note that the substitution for Bi by Pb enhances the orthorhombic distortion so that $\Delta(b-a) = 0.09$ Å instead of 0.03 Å for the nonsubstituted Pb sample. The range of solubility for Ni and Zn in $\text{Bi}_{1.2}\text{Pb}_{0.8}\text{La}_{0.5}\text{Sr}_{1.5}\text{Cu}_{1-x}\text{M}_x\text{O}_6$ is smaller by a factor of about 2 than for $\text{Bi}_2\text{La}_{0.5}\text{Sr}_{1.5}\text{Cu}_{1-x}\text{M}_x\text{O}_6$, since the samples with $x > 0.05$ for Ni and with $x > 0.04$ for Zn are definitely multiphase. Nevertheless, in spite of the smaller solubility range the lattice-parameter changes for both

Ni and Zn substitution reveal the same trends as before with a slight increase in a and b . As in the case of the A-series, TGA measurements show no noticeable changes in the oxygen content due to the substitution. The oxygen content is also found to be independent of the heating treatment (ambient and cooling rate).

Figure 2 shows the variation of the superconducting critical temperatures (as determined by ac-susceptibility measurements by defining the width of the transition, which was in the order of 1 K for all samples, as ΔT between 10% and 90% amplitude of the signal) as a function of the dopant content x . Both Ni and Zn substitution depress the T_c at approximately the same rate (8 K/mol %) at low x . While there is a linear relation for T_c versus x in $\text{Bi}_{1.2}\text{Pb}_{0.8}\text{La}_{0.5}\text{Sr}_{1.5}\text{Cu}_{1-x}\text{Ni}_x\text{O}_6$ across the whole range until the T_c is below 4.2 K, the T_c remains more or less the same for all $x > 0.015$ in $\text{Bi}_{1.2}\text{Pb}_{0.8}\text{La}_{0.5}\text{Sr}_{1.5}\text{Cu}_{1-x}\text{Zn}_x\text{O}_6$ (see Fig. 2). This behavior indicates that the solubility range is limited to 0.02 for Zn in contrast to the value 0.05 for Ni, which is slightly below the limit determined from x-ray-diffraction data. Resistivity measurements for several members of the Zn- or Ni-doped series are displayed in Fig. 3. Only the samples that show metallic behavior are superconducting; if not, they are semiconducting, indicating the absence of the metallic state between the superconducting and semiconducting state, in agreement with previous studies of the 3d-metal-substituted $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_{4-y}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ systems.^{4,10,21} It is interesting to note that none of the Zn- or Ni-doped $\text{Bi}_{1.2}\text{Pb}_{0.8}\text{La}_{0.5}\text{Sr}_{1.5}\text{Cu}_{1-x}\text{M}_x\text{O}_6$ superconducting samples

FIG. 2. Superconducting transition temperatures T_c (as derived by ac susceptibility) for $\text{Bi}_{1.2}\text{Pb}_{0.8}\text{La}_{0.5}\text{Sr}_{1.5}\text{Cu}_{1-x}\text{M}_x\text{O}_6$ ($M = \text{Ni}, \text{Zn}$) as a function of dopant content x .

shows a semiconductinglike behavior above the T_c (usually indicative of inhomogeneities or multiphases), whereas this was quite common for the Y- or La-based systems. It is doubtful that samples of these systems containing six components are more homogeneous than those of the Y- and La-based systems. The difference more likely arises from the presence of small amounts of secondary phases which are metallic for the Bi-based system and semiconducting for the Y- and La-based systems.

Measurements of the Meissner effect show that there is no significant change in the Meissner fraction for both the Ni- and Zn-doped series. However, the signal obtained by Meissner measurements broadens at higher sub-

stitution levels. This is in contrast to the ac-susceptibility and the resistivity measurements, which both show very sharp transitions for the whole range in the Ni- as well as the Zn-doped series. Critical-field measurements were performed on an undoped sample of $\text{Bi}_{1.2}\text{Pb}_{0.8}\text{Sr}_{1.5}\text{La}_{0.5}\text{CuO}_6$ having a T_c of 29 K and a ΔT_c of 1 K. Upon increasing the applied field by steps of 0.5 T up to 5 T we note a broadening of the superconducting transition, but only a small shift (no greater than 1 K) of the superconducting transition. These data indicate that these materials have a high critical field, corresponding to a short coherence length, as observed for the other high- T_c oxides, with the exception of the Nd-based cuprates.

B. Mn-based compounds

We now present results of our studies when Mn is replaced by Ni and Zn in the Mn-based compounds $\text{Bi}_2\text{Sr}_2\text{Mn}_{1-x}\text{M}_x\text{O}_{6+y}$ (C series) and $\text{BiPbSr}_2\text{Mn}_{1-x}\text{M}_x\text{O}_6$ (D series). It is important to remind the readers, that both the C and D series of compounds show crystal structures similar to the A and B series, respectively, with the presence of the structural modulation that is present for the compounds without Pb and which disappears for the compounds containing Pb. Previous studies have shown that in the modulated $\text{Bi}_2\text{Sr}_2\text{MnO}_6$ phases Mn can exist in various oxidation states (+2, +3, and +4),^{22,23} whereas Mn adopts only the oxidation state +3 in the Pb-containing $\text{BiPbSr}_2\text{MnO}_6$ samples.^{24,25}

X-ray powder-diffraction spectra collected for samples of the C and D -series Ni- or Zn-doped manganese-based series could be indexed on the basis of the orthorhombic structures given in the literature.¹⁶ Good agreement between calculated and observed intensities was achieved for both the modulated and nonmodulated structures. The variation of the lattice parameters are shown in Fig. 4. Ni-doped $\text{Bi}_2\text{Sr}_2\text{Mn}_{1-x}\text{M}_x\text{O}_y$ and $\text{BiPbSr}_2\text{Mn}_{1-x}\text{M}_x\text{O}_y$ samples were definitely single phase up to $x = 0.3$ and showed the presence of only a few very weak impurities in the diffraction patterns for $x = 0.4$ and 0.5 . In contrast, for the Zn-doped series weak impurity lines were observed already for $x = 0.3$, indicating as observed previously for the Cu-based compounds that the solubility range is smaller for the Zn-doped than for Ni-doped samples. A striking difference, however, with the Cu-based compounds is that the solubility range for Ni or Zn in the Mn-based compounds is larger by a factor 10.

We present the crystallographic data [Fig. 4(b)] for the $\text{BiPbSr}_2\text{MnO}_6$ series that is structurally modulation free and contains only Mn^{3+} . The orthorhombic distortion characterized by the splitting between the lattice parameters a and b remains constant through the range of solubility. But, the lattice parameters a and b increase upon increasing both the Ni and Zn doping in contrast to the lattice parameter c that decreases for both series with a faster decrease for the Ni-doped than for the Zn-doped samples. The observation that the lattice parameters a , b , and c are constant for $x > 0.2$ in $\text{BiPbSr}_2\text{Mn}_{1-x}\text{Zn}_x\text{O}_6$ and $x > 0.3$ in $\text{BiPbSr}_2\text{Mn}_{1-x}\text{Ni}_x\text{O}_6$ suggests, like the oc-

FIG. 3. The temperature dependence of the resistivity for some selected samples of the $\text{Bi}_{1.2}\text{Pb}_{0.8}\text{La}_{0.5}\text{Sr}_{1.5}\text{Cu}_{1-x}\text{M}_x\text{O}_{6+y}$ series with $M = \text{Ni}$ (top) and $M = \text{Zn}$ (bottom).

FIG. 4. Unit-cell parameters (a , b , c , and V) as a function of dopant content x in (a) $\text{Bi}_2\text{Sr}_2\text{Mn}_{1-x}\text{M}_x\text{O}_{6+y}$ and (b) $\text{BiPbSr}_2\text{Mn}_{1-x}\text{M}_x\text{O}_6$ with $M=\text{Ni}$ (triangles) and $M=\text{Zn}$ (circles). Note that in the case of (a) the lattice constant a corresponds to that of the subcell ($=a/4$ of the whole cell).

currence of the impurity lines in the x-ray-diffraction spectra, that the solubility range is limited to 0.2 for Zn and 0.3 for Ni.

The lattice parameter a represents the distance between two Mn atoms within the MnO_2 planes. Thus, by replacing Mn^{3+} in the high-spin state ($r=0.65$ Å) by a larger ion such as Ni^{2+} of atomic radius 0.69 Å or Zn^{2+} of atomic radius 0.74 Å, one would expect an increase in the lattice parameter a as observed experimentally. The 3d metal is located at the center of an oxygen octahedron and an increase in the basal-plane distance a results in a compression of the octahedron along the c axis (i.e., a decrease of the lattice parameter c) consistent with our x-ray data. The Ni and Zn substitution involves the replacement of a trivalent ion (Mn^{3+}) by a divalent ion (Ni^{2+} or Zn^{2+}). Thus, to maintain charge balance the oxygen content should decrease with increasing substitution. TGA measurements performed on several Ni- and Zn-doped samples (which fail to give accurate absolute values but can detect relative changes) have revealed a significant trend: a decrease of the oxygen content occurs with increasing substitution concentration for both Ni and Zn, as expected from simple valence considerations.

We turn to the crystallographic data for the Ni- and Zn-doped $\text{Bi}_2\text{Sr}_2\text{MnO}_z$ series whose structure contains four different crystallographic Mn sites with Mn in various oxidation states. Figure 4(a) shows the variation of the lattice parameters for this series. Upon Ni or Zn substitution in the $\text{Bi}_2\text{Sr}_2\text{MnO}_z$ phase the lattice parameters a and b progressively converge so that the orthorhombic distortion appears to be quite small around $x=0.4$. At

the same composition the samples were also found to become multiphase. Finally, Fig. 4(a) shows that upon Zn or Ni substitution the unit-cell volume and lattice parameter c slightly increase in contrast with the c -axis compressions observed for the $\text{BiPbSr}_2\text{MnO}_6$ series. In the Pb-doped compounds the divalent Ni and Zn ions substituted for the only existing trivalent Mn ions whereas for the samples without Pb they can substitute for Mn^{2+} , Mn^{3+} , and Mn^{4+} . From size considerations both Ni^{2+} ($r=0.69$ Å) and Zn^{2+} ($r=0.74$ Å) are expected to replace Mn^{3+} ($r=0.65$ Å) rather than Mn^{2+} ($r=0.83$ Å) or Mn^{4+} ($r=0.53$ Å) (these values are for 3d metals in their high-spin configuration). From valence considerations, one would expect that divalent Ni and Zn ions substitute for the divalent Mn^{2+} ions. In this case, because of the large size of Mn^{2+} compared with Ni^{2+} or Zn^{2+} one would expect a decrease of the lattice parameter a resulting in an elongation of the octahedron along the c axis (i.e., an increase in the lattice parameter c). Slight decreases in the average a - and b -lattice-parameter changes $[(a+b)/2]$ and the slight increase in the lattice parameter c measured upon Ni or Zn substitution seem to favor the substitution for Mn^{2+} by Ni^{2+} or Zn^{2+} . If both divalent Zn and Ni replace Mn^{3+} , as initially assumed, the oxygen content of $\text{Bi}_2\text{Sr}_2\text{Mn}_{1-x}\text{M}_x\text{O}_y$ has to change, in order to maintain charge balance, whereas it will remain constant if Zn and Ni replace Mn^{2+} . No noticeable changes in the oxygen content with increasing Ni or Zn substitution could be determined by TGA. That, together with the fact that we could not observe any change in the modulation, seems to favor the substitution

of Zn or Ni for Mn^{2+} . Future neutron experiments will be necessary in order to resolve this point conclusively.

MAGNETISM

We have shown that the modulated $\text{Bi}_2\text{Sr}_2\text{MnO}_y$ phase orders antiferromagnetically at 120 K. At this temperature, there is a sharp rise in the susceptibility (due to a weak ferrimagnetism induced by the structural modulation),^{17,22} whereas the nonmodulated $\text{BiPbSr}_2\text{MnO}_6$ phase orders antiferromagnetically at higher temperatures (T_N between 150 and 190 K) with a less-pronounced peak in the susceptibility consistent with the absence of the structural modulation.^{24,25} Both compounds are two-dimensional (2D) antiferromagnetic insulators, where the separation between the MnO_2 layers is large.

We have measured how the T_N changes upon Ni or Zn doping in the C and D series. Figure 5 displays the variation of the susceptibility as a function of the temperature for several members of the $\text{BiPbSr}_2\text{Mn}_{1-x}\text{M}_x\text{O}_6$ series. The measurements were taken at a field of 3 kG on warming and cooling after the samples have been cooled to 4.2 K in zero field. For both Ni- and Zn-doped samples [Figs. 5(a) and 5(b), respectively] the susceptibility cusp corresponding to the 3D antiferromagnetic ordering shifts towards low temperatures upon increasing dopant content with a decrease faster for Zn [$dT_N = 30 \text{ K}/(10 \text{ at. } \%)$] than for Ni [$dT_N = 5\text{--}8 \text{ K}/(10 \text{ at. } \%)$]. This phenomena can be explained in several ways: Replacing a Mn^{3+} ion with spin $S=2$ by a Ni^{2+} ion with spin $S=1$ decreases the exchange interactions and thereby the 3d antiferromagnetic ordering T_N (which depends on the spin S). The replacement of Mn by a nonmagnetic ion (with spin $S=0$) such as Zn is expected to weaken even more the intralayer coupling than the substitution by Ni, thereby leading to a stronger decrease in T_N for increasing dopant content for the Zn- than for the Ni-doped series as observed experimentally. On the other hand, the decrease in T_N can also be related simply to the fact that in both Zn and Ni substitution the 2D correlation in the planes is disrupted by the substituent, which results in a decrease of the 3D ordering temperature T_N . In the case of the dopant Zn the effect of disorder on suppressing the transition temperature T_N has to be much stronger, because of the lack of any magnetic superexchange. In the case of the dopant Ni, which allows superexchange, the disorder may result mainly from the fact that contrary to Mn where spins are always aligned perpendicular to the plane, the spins can also be aligned in the plane as known from the La_2NiO_4 case.

For these materials which are 2D in nature, we should also observe a broad maximum in the susceptibility at temperatures much larger than T_N . For instance, in La_2CuO_4 , which has a T_N of about 200 K, the 2D ordering was deduced from the broad maximum in the temperature dependence of the susceptibility which occurs below 1000 K. The susceptibility of the undoped sample (Fig. 5) decreases slightly from room temperature to go through a minimum just before T_N . The increase of the susceptibility with increasing temperature up to 300 K may suggest that the 2D correlation develops at relatively

FIG. 5. Temperature dependence of the magnetic susceptibility for several members of the $\text{BiPbSr}_2\text{Mn}_{1-x}\text{M}_x\text{O}_6$ series with $M = \text{Ni}$ (top) and $M = \text{Zn}$ (bottom). The applied magnetic field was 3 kG.

low temperatures. With increasing either Ni- or Zn-dopant content in these materials this feature is completely overwhelmed and replaced by an increase in the susceptibility with decreasing temperature, suggesting either that it has been shifted to higher temperatures (which would be inconsistent with the observed decrease in T_N), or that by introducing disorder within the magnetic MO_2 sheets the 2D correlations have been suppressed.

Figure 6 shows the variation of susceptibility as a func-

FIG. 6. The temperature dependence of the magnetic susceptibility as a function of dopant content x is shown for several members of the $\text{Bi}_2\text{Sr}_2\text{Mn}_{1-x}\text{Zn}_x\text{O}_{6+y}$ series.

FIG. 7. The antiferromagnetic ordering temperature T_N is plotted as a function of dopant content x for both the $\text{Bi}_2\text{Sr}_2\text{Mn}_{1-x}\text{M}_x\text{O}_{6+y}$ and $\text{BiPbSr}_2\text{Mn}_{1-x}\text{M}_x\text{O}_6$ series with $M = \text{Ni}$ and Zn .

tion of the temperature for the Zn-doped $\text{Bi}_2\text{Sr}_2\text{MnO}_z$ series. As before, T_N decreases with increasing Zn-dopant content. A main difference—which may result from the fact that the structure is modulated—however, is the absence of a minimum in the susceptibility just before the 3D ordering temperature. The variation in T_N upon Ni substitution for the same sample is plotted in Fig. 7. Note that the rate at which T_N decreases is faster when Mn is replaced by Zn than by Ni as observed for the Mn-based samples containing Pb.

DISCUSSION

Substitution by either a magnetic (Ni^{2+}) or a nonmagnetic (Zn^{2+}) transition metal in various Bi-based layered oxides (Fig. 8) has yielded several interesting observations: (1) The range of solubility of Ni and Zn dopants in the Cu-based compounds $\text{Bi}_2\text{La}_{0.5}\text{Sr}_{1.5}\text{Cu}_{1-x}\text{M}_x\text{O}_y$ and $\text{Bi}_{1.2}\text{Pb}_{0.8}\text{La}_{0.5}\text{Sr}_{1.5}\text{Cu}_{1-x}\text{M}_x\text{O}_y$ is significantly lower (about 3–8 times) than in the Mn-based insulating compounds $\text{Bi}_2\text{Sr}_2\text{Mn}_{1-x}\text{M}_x\text{O}_y$ and $\text{BiPbSr}_2\text{Mn}_{1-x}\text{M}_x\text{O}_y$ ($M = \text{Ni}, \text{Zn}$). (2) Within the Cu- or Mn-based compounds, the range of solubility for Zn is always significantly lower than that for Ni. (3) The range of solubility for Ni or Zn is independent of whether or not

FIG. 8. Range of solubility for Ni and Zn in various Bi-based layered compounds with the 2:2:0:1 structure.

the host material has a modulated or nonmodulated structure, all of which leads us to conclude that the range of solubility of the 3d metals not only depends on the nature of the dopant, but also on the nature of the transition metal they have to replace with the main result that electronic rather than structural effects govern the limit of solubility.

The smaller amount of the Zn dopant compared with the Ni dopant that can be substituted for the 3d metal in the structures might be limited by the stability of the expanding unit-cell volume beyond a certain limit, consistent with the fact that Zn^{2+} is larger than Cu^{2+} , Ni^{2+} , and Mn^{3+} . However, a more likely possibility is that these solubility limits are established by the thermodynamics of the competing phases, so that at different formation temperatures the solubility ranges might be different for Ni and Zn. We have carried out experiments in this direction and found that the range of temperature over which these compounds form is very narrow (less than 100°C), thus limiting any conclusions that can be made with respect to the change in solubility as a function of the annealing temperature.

The large difference in Ni or Zn solubility between the Cu- and Mn-based compounds, however, cannot be explained only in terms of the difference in ionic radii. A major relevant difference between the Cu- and Mn-based compounds lies in their different oxidation-reduction behavior (i.e., in their ability to change their valence) in oxide compounds. Whereas oxide compounds having Mn ions in oxidation states 2+, 3+, and 4+ are quite common, compounds in which the oxidation state of Cu is 3+ are rare and most, like LaCuO_3 or $\text{La}_2\text{Cu}_{0.5}\text{Li}_{0.5}\text{O}_4$ must be synthesized under high pressure. In $\text{Bi}_2\text{La}_{0.5}\text{Sr}_{1.5}\text{CuO}_y$ or $\text{Bi}_{1.2}\text{Pb}_{0.8}\text{La}_{0.5}\text{Sr}_{1.5}\text{CuO}_6$ the formal valence of Cu is, as reported elsewhere, 2.23 (Ref. 20). When a divalent ion is substituted for Cu in these materials, so as to maintain charge balance, the remaining Cu ions have to be oxidized (i.e., the Cu valence has to increase) or the oxygen content has to decrease. Studies of the $\text{Bi}_{1.2}\text{Pb}_{0.8}\text{La}_{0.5}\text{Sr}_{1.5}\text{CuO}_6$ phase have shown that this compound cannot exist for oxygen stoichiometries lower than 6, leaving the oxidation state of Cu as the only possibility to compensate for the charge unbalance created by the Ni or Zn substitution. Thus, it is the difficulty in oxidizing Cu that limits the solubility range of Ni or Zn in these materials. In contrast, for the Mn-based materials, Mn can easily be oxidized to Mn^{3+} or Mn^{4+} . Therefore the solubility range for Ni or Zn is expected to be larger, as observed experimentally.

The finding that doping with both Zn and Ni suppresses the T_c in the 25-K $\text{Bi}_{1.2}\text{Pb}_{0.8}\text{La}_{0.5}\text{Sr}_{1.5}\text{CuO}_6$ phase at approximately the same rate (8 K/at. %) with no difference between magnetic and nonmagnetic ions, leads to the conclusion that this system behaves similarly to the Y-Ba-Cu-O or La-Sr-Cu-O systems. Thus, in the 25-K Bi-based cuprates, as for Y-Ba-Cu-O or La-Sr-Cu-O, disorder plays a major role in depressing the T_c . It is interesting to recall that for the 25-K Nd-Ce-Cu-O cuprate (a chemical system identical to the Bi-based phase) magnetic impurities have been found to depress the T_c faster than nonmagnetic impurities as in conventional super-

conductors. We should emphasize that in spite of belonging to the same chemical system (cuprates) and having the same T_c these materials have a quite different coherence length, as suggested by critical-field measurements [$dT_c/dH = 1$ K/(5 T) for $\text{Bi}_{1.2}\text{Pb}_{0.8}\text{La}_{0.5}\text{Sr}_{1.5}\text{CuO}_6$ and 20 K/(5 T) for $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$]. Determining the origin of such a difference could be an important step in understanding the pairing mechanism in the high- T_c oxides.

Finally with respect to the antiferromagnetic ordering in the $\text{Bi}_2\text{Sr}_2\text{MnO}_y$ and $\text{BiPbSr}_2\text{MnO}_y$ compounds that is yet not fully understood, we show (Fig. 7) (1) that substitution for Mn by Ni suppresses the T_N more slowly than the substitution by Zn and (2) that within the same dopant the depression of T_N is independent of whether the structure of the host compound is modulated or not. As expected, the influence of the nonmagnetic $3d^{10}$ ele-

ments Zn^{2+} with spin $S=0$ is much more drastic than that of the magnetic $3d^8$ Ni^{2+} (with spin $S=1$). We believe that it is the decrease in the magnetic spin of the substituted ion combined with the disorder introduced by the substitution, which leads to a shortening of the in-plane 2D correlation length, thereby shifting the 3D antiferromagnetic ordering temperature to lower temperatures.

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