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High-pressure study of $R\mathrm{Sr_2Cu_{2.7}Mo_{0.3}O}_y$ with R =Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb

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The hydrostatic-pressure effect on the superconducting transition temperature (T_c) of the stabilized Sr-based 1:2:3 compounds $R\mathrm{Sr_2Cu_{2.7}Mo_{0.3}O}_y$ with R=Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb has been determined up to 16 kbar. All T_c's are enhanced linearly by pressure at a rather rapid rate (dT_c/dP). A drastic jump in dT_c/dP vs ionic radius of R occurs near *Dy*, i.e., $dT_c/dP \sim 0.7$ K/kbar for small R=Ho, Er, Tm, and Yb, and ~0.4 K/kbar for the larger R's=Tb, Gd, Eu, and Sm. The results suggest that Cu(1) substitution by Mo is crucial in the stabilization of the Sr-based 1:2:3 compound. Several possibilities for the dT_c/dP step detected are advanced.

I. INTRODUCTION

The simultaneous occurrence of a strong superconducting interaction and lattice instabilities has long been recognized.[1] A close correlation between these two phenomena has been proposed in the conventional low-temperature superconductors. The lattice instabilities detected in these compounds have been attributed to the unusual characteristics of the phonon and/or electron energy spectrum. The general appearance of high-temperature superconductivity (HTS) in compounds near their metal-insulator phase boundary seems to suggest a possible interplay between HTS and lattice (or other type) instabilities.[2] By examining their solid-state chemistry properties, it was indeed proposed[3] that high-temperature superconductors (HTS's) might have already reached the lattice-stability limit. The study of the structural stability in HTS's and related materials will, therefore, shed important light on the occurrence of HTS and on the formation of HTS's as well.

Despite the chemical similarity between Sr and Ba, the 1:2:3 structure for HTS can only be stabilized at ambient pressure using the standard solid-state reaction technique in the Ba-based $R\mathrm{Ba_2Cu_3O_7}$ (RBCO) compounds[4] but not in the Sr-based $R\mathrm{Sr_2Cu_3O_7}$ (RSCO) ones, when R =Y, La, or any of the other rare-earth elements except Ce and Tb. A superconducting transition with an onset temperature (T_{co}) up to 80 K was reported[5] earlier in a multiphase sample with a nominal composition of YSrCuO_x which was synthesized by rapid quenching in air from 1300 °C to room temperature. Unfortunately, later efforts[6] failed to reproduce the observation. On the other hand, under a pressure of 7 GPa at 1380 °C, single-phase RSCO samples with R =Y were successfully synthesized[7] and exhibited a $T_{co} \sim 60$ K with a resistivity ρ vanishing only below 20 K. In an alternate approach,[8–10] partial substitution of Fe, Ti, Al, Co, Ga, Pb, Nb, and Ta for Cu led to the stabilization of the RSCO phase at ambient pressure. However, superconductivity with a $T_{co} \leq 50$ K was detected[10] only in some of these doped RSCO compounds when prepared using the hot-isostatic press technique. Later, preliminary results showed[11] that partial replacement of Cu by Mo also stabilizes the 1:2:3 phase in $\mathrm{YSr_2Cu_3O_7}$ at ambient pressure, and that $\mathrm{YSr_2Cu}_{3-x}\mathrm{Mo}_x\mathrm{O}_y$ samples with x =0.3 become superconducting with a $T_{co} \sim 40$ K and a zero resistivity ρ near 20 K. Recently, the complete series of single-phase $R\mathrm{Sr_2Cu}_{3-x}\mathrm{Mo}_x\mathrm{O}_y$ [RS(CM)O] with x =0.3 was[12] successfully synthesized for R representing all rare-earth elements except Ce and Lu. Apparently, the stability range for x is very narrow. These compounds have a T_c centering around 30 K, except for R =La, Pr, and Nd which are not superconducting. The role of Mo doping in the stability of RS(CM)O is unknown.

In an attempt to unravel the role of Mo in the formation of the 1:2:3 structure in RS(CM)O samples and the reason for their lower T_c than that of RBCO, we have examined the hydrostatic pressure effect on T_c (dT_c/dP) of the superconducting RS(CM)O compounds. We found that T_c is enhanced by pressure for all compounds with a relatively large dT_c/dP and that dT_c/dP for compounds whose rare-earth element has an ionic radius smaller than that of Dy is ~0.7 K/kbar, and drastically drops to ~0.4 K/kbar for those with a larger radius. By comparing our observations with the previous pressure data on doped RBCO's, we conclude that Cu-chain site doping by Mo is crucial in the stabilization of the 1:2:3 phase of RSCO, enabling a better match with the ionic radii of the constituents. We also propose that the disorder associated with the Mo dopant in these Mo-doped RSCO compounds is the main cause for their depressed T_c and that the possible site mixing and/or some electronic transition may be responsible for the sudden decrease in dT_c/dP observed in the compounds of R with ionic radius smaller than that of Dy. Such a proposition is in accord with the previous structure data of similar compounds[9] and our preliminary results on the oxygen content of Mo-stabilized RS(CM)O's.

II. EXPERIMENT

Polycrystalline samples of $R\mathrm{Sr_2Cu_{2.7}Mo_{0.3}O}_y$ with R =Yb, Tm, Er, Ho, Dy, Tb, Gd, Eu, and Sm were prepared by a solid-state reaction. High-purity powders of $R_2\mathrm{O}_3$ (except for R =Tb, where $\mathrm{Tb_4O_7}$ was used), $\mathrm{SrCO_3}$, CuO, and Mo were thoroughly mixed in appropriate proportions. The mixed powder was compacted and fired for ~3 h at 1000–1050 °C in an O_2 atmosphere, flowing at a rate of 250–500 cc/min. It was then slowly cooled to room temperature for ~14 h. The samples were characterized by powder x-ray-diffraction and magnetization measurements to ensure the high quality of the samples studied. The Mo content chosen in that manner was found to give the best phase purity and the narrowest magnetic transition based on the above synthesis conditions. Bars of dimensions $\sim 4\times 1\times 0.5$ mm^3 were cut from the pellets for ρ measurements. Platinum leads were pressure attached to the samples with In contacts. A standard four-probe technique was employed at 16 Hz to determine ρ. The temperature was measured with a Chromel-Alumel thermocouple and/or a Ge thermometer in different temperature ranges. The hydrostatic-pressure environment was provided by a modified Be-Cu high-pressure technique with a Teflon cell using 3*M* Fluorinert fluid as the pressure medium. The pressure was determined by a superconducting Pb barometer placed next to the sample inside the high-pressure cell.

III. RESULTS AND DISCUSSION

All samples examined in the present investigation were single phase within the x-ray powder-diffraction resolution. They had T_c centers between 30 and 36 K with a width of ~3–10 K. The onset and midpoint transition temperatures (T_{co} and T_{cm}) are shown in Fig. 1 for the RS(CM)O studied as a function of the ionic radius of *R*. Under pressure, both T_{co} and T_{cm} are enhanced linearly and reversibly while ρ is suppressed. Typical results are exemplified by the case for $R=$Tb in Fig. 2. The variations dT_{co}/dP and dT_{cm}/dP as a function of the ionic radius of *R* are displayed in Fig. 3. It is evident that both dT_{co}/dP and dT_{cm}/dP undergo a drastic drop around Dy and vary only slightly with the ionic radius in the two regions separated by Dy. Since dT_{co}/dP and dT_{cm}/dP vary with the ionic radius of *R* in a similar fashion, we shall use the term dT_c/dP in a later discussion of these results.

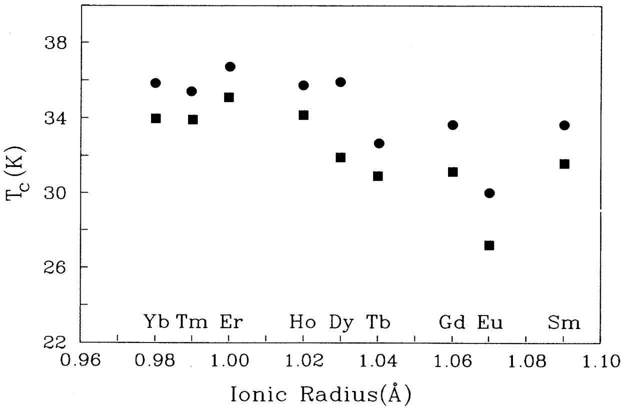

FIG. 1. The T_{co}(●) and T_{cm} (■) of the superconducting transitions of RS(CM)O's at ambient pressure and as a function of the ionic radius of *R*.

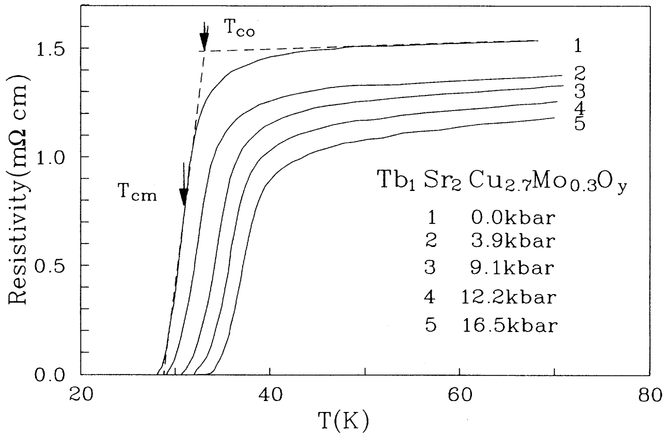

FIG. 2. The pressure effect on $\rho(T)$ of $TbSr_2Cu_{2.7}Mo_{0.3}O_y$.

The pressure effect on the T_c of HTS's has been studied extensively. Some of the studies[13–20] focused on the doped RBCO's through cation or anion doping. In the case of $YBa_2Cu_{3-x}X_xO_{7-\delta}$ [YB(C*X*)O], the dopant *X* can enter the CuO chain (Cu1) or the Cu plane (Cu2) sites, and oxygen tends to come off the chain sites (O1) more easily than it leaves the CuO_2-plane sites (O2 and O3). Both the introduction of *X* to $YBa_2Cu_3O_7$ (YBCO) and the removal of O from YBCO suppress the T_c. Such T_c suppression can be attributed to the transfer of charge between the active CuO_2 planes and their surroundings when the Cu1 or the O1 site is perturbed, or to the disorder due to substitution of *X* for Cu2. The application of pressure has been shown[20] to result in a charge transfer and to restore the hole-carrier reduction induced by doping or O variation. However, it is very difficult to change the disorder density in the compounds by applying pressure. As a result, one would expect to see a larger dT_c/dP in YB(CX)O when *X* enters the Cu1 site or O is removed from the O1 site than if *X* enters the Cu2 site.

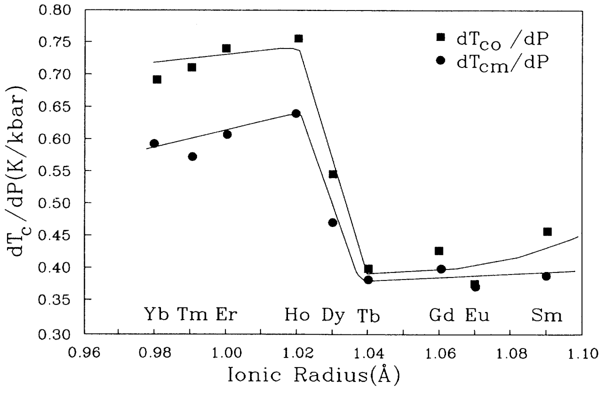

FIG. 3. The ionic-radius dependence of dT_{co}/dP and dT_{cm}/dP of RS(CM)O's.

Indeed, this was observed[13] in YB(C*X*)O when $X=\mathrm{Fe}$, Al, Co, Ni, and Zn. The value of dT_c/dP for X denoting trivalent Fe, Al, or Co which replaces Cu in the Cu1 site is positive, large, and increases with x, whereas dT_c/dP for X denoting divalent Ni or Zn which replaces Cu in the Cu2 site is negligible and weakly dependent on x. The value of dT_c/dP is also positive and large for O-deficient YBCO where vacancies occur at the O1 sites. We have summarized the available low-pressure (<20 kbar) $d\ln T_c/dP$ data on doped and undoped 1:2:3 compounds in Fig. 4, as a function of their T_c's. The data points clearly fall into two bands: the upper band represents cation doping into the Cu1 sites or anion doping into the O1 sites and the lower one represents cation doping into the Cu2 site. The $d\ln T_c/dP$ value of RS(CM)O samples of the present study all fall into the upper band, suggesting that the dopant Mo mainly substitutes for the Cu in the Cu1 site to stabilize the 1:2:3-phase RSCO compounds.

The powder x-ray-diffraction results show that all RS(CM)O's examined display a tetragonal symmetry, instead of the orthorhombic one characteristic of the stoichiometric RBCO's. This suggests a Cu1 substitution by Mo in RS(CM)O's. It is known that the orthorhombic symmetry of the stoichiometric RBCO's results from O ordering in the CuO chains. Therefore a random Cu1-site substitution is expected to remove the orthorhombic distortion as has been demonstrated[21] for $x>0.1$ in YB(C*X*)O with $X=\mathrm{Fe}$, Co, and Al. This is in strong contrast to a Cu2-site substitution[21] where the orthorhombic symmetry remains within the homogeneity range for YB(C*X*)O with $X=\mathrm{Ni}$ and Zn. Our suggestion is also consistent with our preliminary O-content measurements on $\mathrm{TbSr_2Cu_{2.7}Mo_{0.3}O_{7-\delta}}$. We found that the δ does not change significantly, i.e, $\Delta\delta \leq 0.1$, over a wide temperature range between 400 and 700 °C, indicating a strong bond between the O in the CuO chain and its surroundings. This is very similar to $\mathrm{YBa_2Cu_{3-x}Co_xO_{7-\delta}}$, where Co substitutes for Cu in the Cu1 site,[21] but rather different from the undoped $\mathrm{YBa_xCu_3O_{7-\delta}}$, where O in the CuO chain is only loosely bound.

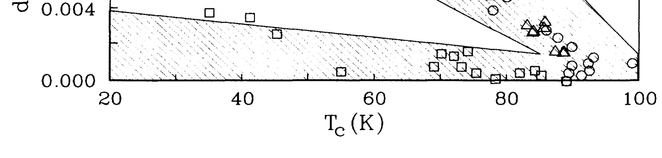

FIG. 4. $d\ln T_c/dP$ vs T_c for undoped and doped 1:2:3 compounds. ▼, present work; ○, O1-site doping (Refs. 16–19); △, Cu1-site doping (Refs. 13–15); and □, Cu2-site doping (Refs. 13–15).

It is known that lattice matching is an important factor in the formation of HTS compounds. The much smaller size of Sr than that of Ba clearly is responsible for the structural instability of the 1:2:3 phase in RSCO. The partial replacement of Cu (~0.62 Å) by the smaller Mo (~0.42 Å) seems natural for the stabilization of the 1:2:3 RSCO by reducing the mismatch among the various constituent elements. To understand further how partial Cu1 substitution by Mo can lead to the stabilization of the 1:2:3 structure in RSCO, we compared the neutron-diffraction data[22] of $\mathrm{YBa_2Cu_3O_7}$ with that[9] of $\mathrm{LaSr_2Cu_2GaO_7}$ [LaS(CG)O] where all Cu1 sites are supposed to be occupied by Ga. An important difference emerges concerning the O1 position. In YBCO, Ba is tenfold coordinated with the four short bonds (~2.741 Å) and the two long bonds (~2.877 Å for orthorhombic YBCO) to the two O1 atoms, in addition to the four intermediate bonds to the O atoms in the $\mathrm{CuO_2}$ planes. For LS(CG)O, Sr becomes ninefold coordinated with the O1 atoms moving away from the CuO chain to directly beneath the Sr atoms (apex sites) by replacing the two longest bonds in YBCO with a very short bond (~2.33 Å) for the displaced O1 atom. According to a simplified valence-summation argument,[23] the shortening of the Sr (apex O) bond will ensure a greater tolerance to the length of other planar Sr-O bonds, and thus will enhance the lattice match among constituent elements and the affinity of the displaced O1 atoms to their surroundings.

The dramatic jump in dT_c/dP shown in Fig. 3 can be explained in terms of several possibilities. In spite of the jump, all $d\ln T_c/dP$ values fall into the upper band displayed in Fig. 4. This appears to rule out the possibility of a major Cu2-site substitution for large $R=\mathrm{Tb}$, Gd, Eu, and Sm. The high-pressure results on $\mathrm{YSr_2Cu_{2.8}Mo_{0.2}O}_y$ and $\mathrm{TbSr_2Cu_{2.7}Mo_{0.3}O}_y$ were compared[24] and briefly reported. In that paper, the important role of Cu1 in the stabilization of the 1:2:3 RSCO's was pointed out, and a possible partial Cu2 substitution in $\mathrm{TbSr_2Cu_{2.7}Mo_{0.3}O}_y$ was also suggested. The dT_c/dP drop observed here can be attributed to this possible multisite (Cu1 and Cu2) doping by Mo atoms. Based on ionic-radius considerations, the $\mathrm{CuO_2}$ planes are under stress in the RS(CM)O's. Therefore, it is easier for some Mo atoms to enter the Cu2 sites to relieve the stress and thus reduce the dT_c/dP in those RS(CM)O's with larger $R=\mathrm{Tb}$, Gd, Eu, and Sm. The other possibility is associated with possible site mixing between larger R's and Sr. It was demonstrated[9] that site mixing occurs in $R\mathrm{Sr_2Cu_2GaO_{7-\delta}}$ for the larger $R=\mathrm{La}$ but not the smaller $R=\mathrm{Ho}$. Such site mixing changes the character of charge transfer between the $\mathrm{CuO_2}$ layer and its surroundings and thus results in a smaller dT_c/dP. While the possibilities about doping various sites can describe the general decrease of dT_c/dP as R becomes larger and the general suppressed T_c of RS(CM)O, it cannot account for the drastic drop in dT_c/dP near Dy and the nearly constant dT_c/dP away from Dy. This leads us to the proposition of a possible electronic transition where the electron energy spectrum of RSCO may depend sensitively on the ionic radius of R.

IV. CONCLUSION

The pressure effect on T_c of RS(CM)O's has been measured up to 16 kbar. The generally large and positive dT_c/dP of these compounds suggests an important role of Cu1 substitution by Mo in the stabilization of the Sr-based 1:2:3 structure. Such a suggestion is in agreement with the present and previous structural data on both the undoped and doped Sr- and Ba-based 1:2:3 compounds. The drastic jump in dT_c/dP observed as a function of the ionic radius of R in RS(CM)O near R =Dy is intriguing. Several possible explanations such as partial Cu2 substitution by Mo for larger R's, site mixing between larger R's and Sr, and an electron transition have been proposed to account for such a drastic dT_c/dP drop and the general suppressed T_c of RS(CM)O. Further study is underway to examine if an orthorhombic phase of RS(CX)O can be stabilized and if dT_c/dP depends on the Mo-dopant level to further reveal the formation of HTS's and the occurrence of HTS.

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