

Strong rare-earth size dependence of T_c in $RSr_2Cu_{2.85}Re_{0.15}O_z$

M. Murugesan

Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400 076, India

M. S. Ramachandra Rao, L. C. Gupta, and R. Pinto

Tata Institute of Fundamental Research, Homi Bhabha Road, Bombay 400 005, India

M. Sharon

Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400 076, India

R. Vijayaraghavan

Tata Institute of Fundamental Research, Homi Bhabha Road, Bombay 400 005, India

(Received 25 August 1995; revised manuscript received 10 October 1995)

We report a strong rare-earth size dependence of T_c in $RSr_2Cu_{2.85}Re_{0.15}O_z$ (R =rare earth, $z \approx 7.2$) compounds, unlike in $RBa_2Cu_3O_y$ compounds. A strong correlation is observed between the superconducting transition temperature and the orthorhombicity of the structure, which itself is R -size dependent. Orthorhombicity is highest for $HoSr_2Cu_{2.85}Re_{0.15}O_z$ and $ErSr_2Cu_{2.85}Re_{0.15}O_z$ compounds, which also have yielded the highest T_c (≈ 42 K). Significantly, $TbSr_2Cu_{2.85}Re_{0.15}O_z$ stabilizes in a 1-2-3 structure and also superconducts ($T_c \approx 22$ K), whereas $EuSr_2Cu_{2.85}Re_{0.15}O_z$ does not superconduct, although it forms a single phase.

I. INTRODUCTION

In general, in a series of superconducting materials in which the rare-earth (R) element is a variable, T_c is observed to be R dependent. Most commonly this arises due to the magnetic interaction of the R moment with the conduction electrons. In addition, R size also may affect T_c . In the high- T_c cuprates $RBa_2Cu_3O_y$, however, T_c is nearly independent of R ions, i.e., independent of the size as well as the magnetic moment of the R ions.¹ We have been on the lookout for those cuprate systems of 1-2-3 structure wherein such effects may be observed. We have observed these effects in $RSr_2Cu_{2.85}Re_{0.15}O_z$.

The orthorhombic layered perovskitelike crystal structure of $YBa_2Cu_3O_{7-\delta}$ is unstable for the composition $YSr_2Cu_3O_z$. Replacement of Ba by Sr causes drastic changes in the bond distances and the 1-2-3 structure becomes unstable. The solid solubility limit of Sr in $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ is in the range $0 \leq x \leq 1.2$, and for $x > 1.2$, the structure could only be stabilized under high-pressure conditions,² resulting in a low T_c (≈ 18 K) with a very broad transition width ($\Delta T \geq 40$ K). An increase in Sr content results in a loss of oxygen from the lattice, leading to a decrease in the stability of the crystal structure and suppression of superconductivity. Thus, there are two aspects which are intimately connected with the substitution of Sr at Ba sites, namely, (i) stability of the crystallographic structure and (ii) superconductivity and its relationship with structure. It has been shown that the orthorhombic layered perovskite-like 1-2-3 structure can be stabilized and superconductivity induced in $YSr_2Cu_3O_z$ by partial replacement of Cu by a number of metal (M) cations (M =Fe, Al, Co, W, Mo, Re, etc.).³⁻⁷ Introduction of M cations into the lattice stabilizes the structure by providing extra oxygen to the crystal lattice to counteract the loss of oxygen caused by Sr substitution at

Ba sites. It should be pointed out that attempts to synthesize compounds with M =Zn and Ni have not been successful.⁴ This is attributed to the fact that both Ni and Zn ions are divalent and, therefore, do not "bring" enough oxygen into the crystal lattice, rendering the lattice unstable.

In order to investigate the effects associated with the structural and superconducting properties as a function of different R ions, we synthesized compounds belonging to the system $YSr_2Cu_{2.85}Re_{0.15}O_z$, where R =La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. It turned out that these materials exhibit a very interesting structure-superconductivity correlation. The purpose of this paper is to report our results on this correlation. Aspects connected with the interplay of superconductivity and magnetism will be presented in our forthcoming publication.

II. EXPERIMENT

Following the solid state synthesis route, polycrystalline compounds of $RSr_2Cu_{2.85}Re_{0.15}O_z$ (R =lanthanides and Y) were prepared starting with high purity ($\geq 99.99\%$) chemicals. In each case, the stoichiometric mixture of the powders was calcined for 12 h at 1000 °C followed by regrinding and pelletization. The pellets were sintered in flowing oxygen at 1055 °C for all rare earths and Y (except for Tm, which was sintered at 980 °C). Pellets were slow cooled to 500 °C (1 °C/min) and annealed for 10 h and then slow cooled (1 °C/min) to room temperature. The phase purity of the compounds was determined by powder x-ray diffraction (XRD). Four probe electrical resistance measurements in the range 300–12 K were carried out using a closed cycle helium cryocooler. ac magnetic susceptibility (in a field of ~ 0.1 Oe and 313 Hz) measurements were carried out using an ac susceptometer.

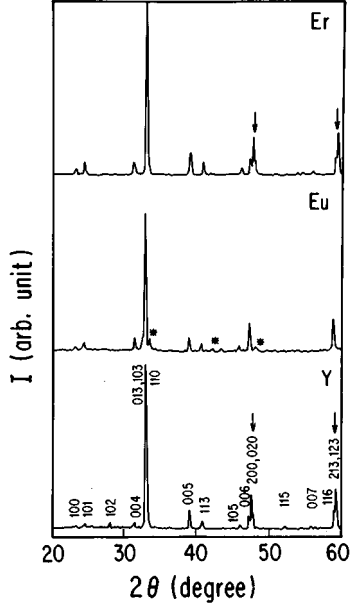


FIG. 1. X-ray diffraction patterns of $RSr_2Cu_{2.85}Re_{0.15}O_z$ ($R=Eu, Er$, and Y). Lines marked by an asterisk do not belong to this phase. Superconductivity sets only in those compounds in which a clear orthorhombic splitting is seen (marked by arrow).

III. RESULTS AND DISCUSSION

XRD patterns obtained on $RSr_2Cu_{2.85}Re_{0.15}O_z$ ($R=Eu, Gd, Tb, Dy, Ho, Er, Tm$, and Y) compounds showed single-phase formation (Fig. 1). Minor impurity peaks (marked with an asterisk) were present for $R=Eu, Gd$, and Tm . All these compounds have orthorhombic crystal structure with a - and b -lattice parameter values quite close to each other (Table I). We must point out here that the material $TbSr_2Cu_{2.85}Re_{0.15}O_z$ is stabilized in the 1-2-3 phase. This is in contrast with the situation in the case of $TbBa_2Cu_3O_z$, which is a multi-phase material and does not stabilize in the 1-2-3 phase.⁸ This behavior perhaps is due to the higher stability of the phase $BaTbO_3$ as compared to that of $TbBa_2Cu_3O_y$. In the case of Sr-based systems, the reverse seems to be true. A similar kind of phase stabilization was reported by Xiong *et al.*⁹ in $TbSr_2Cu_{2.70}Mo_{0.30}O_z$. We strongly believe that Tb ions must be trivalent in this system like other ions such as Y, Gd, Dy, Ho, Er , and Tm . L_{III} -edge studies should be useful to confirm this aspect.

Compounds with $R=La, Ce, Pr, Nd, Sm, Yb$, and Lu were multiphase.

Orthorhombicity in these systems is very small and, hence, is noticeable only in higher angle diffraction lines, leading to splitting of (0 2 0) and (2 0 0) ($2\theta \approx 47^\circ-48^\circ$), and (2 1 3) and (1 2 3) ($2\theta \approx 58^\circ-60^\circ$) reflections. Such an orthorhombic splitting could be seen only in compounds with $R=Tb, Dy, Ho, Er$, and Tm . In compounds with $R=Eu$ and Gd , although XRD patterns confirmed single-phase formation, no such splitting was observed. Thus, these compounds provide “tetragonal” analogs of $RBa_2Cu_3O_7$ compounds. The oxygen content (z) estimated in some $RSr_2Cu_{2.85}Re_{0.15}O_z$ compounds from neutron diffraction studies¹⁰ is $z=7.34$ and 7.14 for $R=Dy$ and Ho , respectively, and $z=7.19$ for $YSr_2Cu_{2.85}Re_{0.15}O_z$ compounds. In Ba-based $RBa_2Cu_3O_{7-\delta}$ compounds, orthorhombicity of the structure is easily established by the clear splitting of diffraction lines (1 0 3) and (0 1 3) ($2\theta \approx 32^\circ-33^\circ$). This shows that orthorhombicity [$e=(b-a)/(b+a)$] in the materials of this study is quite small and the main line reflections (1 0 3) and (0 1 3) ($2\theta \approx 32^\circ-33^\circ$) are not resolved.

A superconducting transition was observed both by resistivity measurement and diamagnetic response. Figure 2 shows normalized resistivity as a function of temperature for various materials. The inset of Fig. 2. shows the ac $\chi(T)$ response of $ErSr_2Cu_{2.85}Re_{0.15}O_y$ compounds, where the diamagnetic signal is very clearly observed. Out of the single-phase materials with $R=Eu, Gd, Tb, Dy, Ho, Er$, and Tm , superconductivity is observed in compounds with $R=Tb, Dy, Ho, Er$, and Tm . T_c is highest in the cases $R=Ho, Er$, and Y . Quite remarkably, not only does the $TbSr_2Cu_{2.85}Re_{0.15}O_z$ compound form, as mentioned above, in a 1-2-3 structure, it superconducts as well. So far, this is the only material with a stoichiometric concentration of Tb that superconducts. Although $GdSr_2Cu_{2.85}Re_{0.15}O_z$ is a single-phase compound, it exhibits semiconducting behavior at high temperature. However, around 25 K, there is a drop in resistance and zero resistance is not observed down to 12 K. For $R=Eu$, the ρ - T curve shows a semiconducting behavior. We could reproduce all the above observations on three different batches of samples.

Figure 3 shows the variation of T_c and orthorhombicity as a function of rare-earth ionic radius. The compounds $HoSr_2Cu_{2.85}Re_{0.15}O_z$, $ErSr_2Cu_{2.85}Re_{0.15}O_z$ and $YSr_2Cu_{2.85}Re_{0.15}O_z$, having a rare-earth ionic radius (IR) in

TABLE I. Unit cell parameters and superconducting transition temperature of single-phase $RSr_2Cu_{2.85}Re_{0.15}O_z$ compounds.

Rare earth	$T_{c, onset}$ (K)	$T_{c, 0}$ (K)	a axis (Å)	b axis (Å)	c axis (Å)	Orthorhombicity $e=(b-a/b+a) (\times 10^{-3})$	Cell vol. (Å ³)
Eu	—	—	3.836	3.836	11.510	0.00	169.431
Gd	25	—	3.830	3.833	11.511	0.47	169.024
Tb	30	22	3.822	3.826	11.507	0.58	168.328
Dy	37	27	3.812	3.819	11.502	0.85	167.478
Ho	51	42	3.807	3.822	11.501	1.99	167.406
Er	51	43	3.806	3.822	11.500	2.11	167.337
Tm	37	23	3.806	3.810	11.510	0.53	166.989
Y	47	41	3.803	3.819	11.516	2.08	167.302

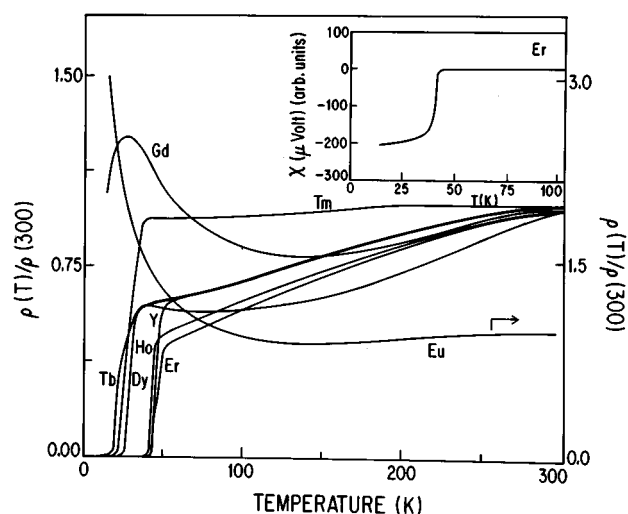


FIG. 2. Resistivity plots of $\text{RSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_z$ ($R=\text{Eu, Gd, Tb, Dy, Ho, Er, Tm, and Y}$). The inset shows the variation of $\chi'(T)$ as a function of temperature in $\text{ErSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_z$ compounds. For $R=\text{Gd}$, only an onset is seen.

the range 1.004–1.019 Å, superconduct with the highest transition temperature [$T_c(\text{max}) \approx 42$ K]. T_c is substantially reduced in compounds with R ionic radius outside this range. For instance, T_c is considerably reduced for Tm [smaller ionic radius ($Tm_{\text{IR}} \approx 0.994$ Å)] and Tb and Dy [larger ionic radius ($Tb_{\text{IR}} \approx 1.040$ Å, $Dy_{\text{IR}} \approx 1.027$ Å)]. This shows that T_c does not vary monotonously as a function of the radius of

the R ions. Orthorhombicity (e), also, like T_c , does not exhibit a monotonous variation with the size of the R ion. Remarkably, T_c and orthorhombicity exhibit a similar trend as a function of R size. A strong correlation between T_c and e is shown in Fig. 3. The inset of Fig. 3 shows the plot of the variation of T_c as a function of orthorhombicity (e) for $\text{RSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_z$ ($R=\text{Tb, Dy, Ho, Er, Tm, and Y}$) compounds. The observed straight line fit also clearly shows that (i) T_c and e vary very similarly as a function of R ionic size; (ii) there exists a strong correlation between e or T_c and R ionic size. It is to be pointed out here that orthorhombicity in $\text{RBa}_2\text{Cu}_3\text{O}_7$ varies monotonously with RE ionic size.¹¹ The following important implications are inferred from the correlation between T_c and e : (1) The magnetic moment of the R ion is not responsible for the depression of T_c . $\text{YSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_z$ (Y has no magnetic moment) and $\text{HoSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_z$ (ground state magnetic moment of $\text{Ho} = 10.63\mu_B$) have nearly the same T_c (≈ 42 K). In fact, the $\text{HoSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_z$ compound has a slightly higher T_c (≈ 42 K) as compared to that of $\text{YSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_z$ ($T_c \approx 41$ K). (2) $\text{EuSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_z$ stabilizes in single phase, although, with much reduced e (≈ 0), and has an oxygen stoichiometry close to 7. This effect is clearly due to the variation in R size; magnetism does not play any role here simply because trivalent Eu ions have $J=0$ and are, therefore, nonmagnetic. This study quite interestingly suggests that in these materials not only having the “right” amount of oxygen content is enough for superconductivity to occur, but also it is essential to have the “right” degree of orthorhombicity.⁶ With decreasing rare-

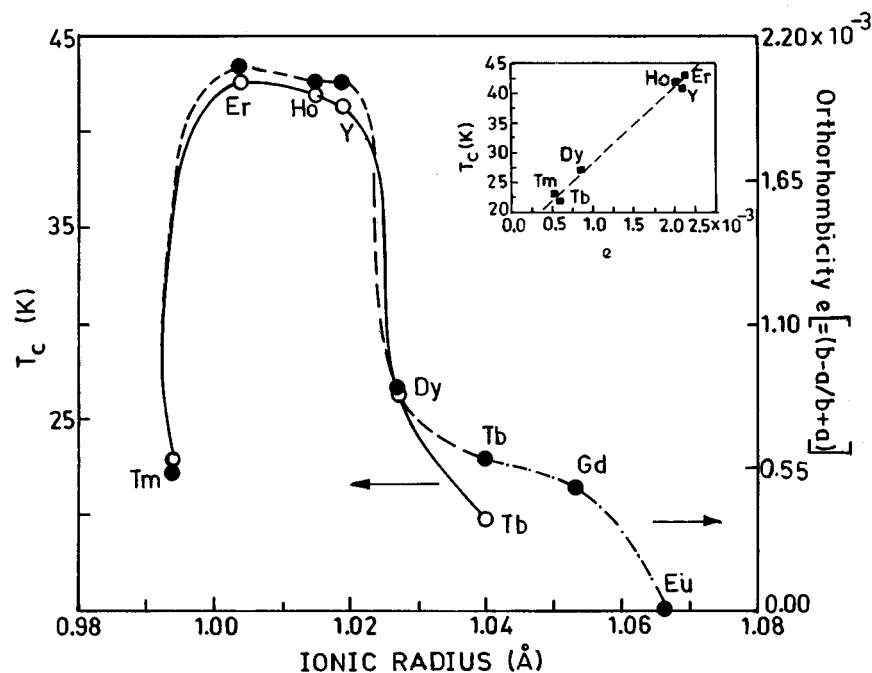


FIG. 3. Variation of T_c and orthorhombicity (e) in $\text{RSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_z$ as a function of rare-earth ionic radius. Compounds for $R=\text{Er, Ho, and Y}$ lie in the plateau region of maximum T_c . A close T_c value of $\text{HoSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_z$ and $\text{YSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_z$ compounds shows that only R size dependence is responsible for the observed T_c variation. The magnetic moment has no role to play. A remarkable feature is the similar trend which T_c and e exhibit as a function of R ionic size. Extension of the (dashed) curve beyond Tb indicates, within the accuracy of our experimental results, that $\text{GdSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_z$ (with a small orthorhombicity) shows only an onset of metallicity (~ 25 K), whereas $\text{EuSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_z$ is tetragonal ($e = 0$) and does not superconduct. The inset shows the variation of T_c as a function of orthorhombicity in $\text{RSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_z$ ($R=\text{Tb, Dy, Ho, Er, Tm, and Y}$) compounds.

earth size from Tb to Dy, T_c increases, attains a maximum value for (Ho, Er, and Y compounds), and then decreases. It is conceivable that this behavior is a manifestation of the variation of the hole density that may occur as a result of subtle variations in bond lengths due to the variation of R size. For example, in $Y_{1-x}Ca_xSr_2Cu_{3-x}M_xO_y$ it has been established that T_c is a function of hole doping which can be varied by varying the Ca concentration.⁷ Thus, Hall-effect measurements should be very informative on this aspect.

We have synthesized a compound $Tm_{0.71}Eu_{0.29}Sr_2Cu_{2.85}Re_{0.15}O_z$ which forms in single phase. The weighted average rare-earth ionic radius in this compound is close to that of Ho [ionic radius ≈ 1.015 Å (Ref. 12)]. On the basis of the dependence of T_c on rare-earth ionic radius as presented above, we expect qualitatively the T_c of this compound to be higher than that of $TmSr_2Cu_{2.85}Re_{0.15}O_z$ ($T_c = 23$ K) and $EuSr_2Cu_{2.85}Re_{0.15}O_z$ (semiconducting). *It is instructive to note that T_c of the above mixed composition is considerably high (≈ 34 K). This is consistent with the results presented above.*

IV. CONCLUSION

In conclusion we have presented results of our studies on the single-phase compounds of $RSr_2Cu_{2.85}Re_{0.15}O_z$ ($R = Eu, Gd, Tb, Dy, Ho, Er, \text{ and } Tm$). Superconductivity is observed in compounds with $R = Tb, Dy, Ho, Er, \text{ and } Tm$. Compounds with $R = La, Ce, Pr, Nd, Sm, Yb, \text{ and } Lu$ are

multiphase. In the superconducting compounds, T_c varies strongly as a function of the size of the R ion. Interestingly, orthorhombicity also exhibits a similar trend as that of R size. This brings out a remarkable relationship between T_c and orthorhombicity. Two other interesting results are that (1) $TbSr_2Cu_{2.85}Re_{0.15}O_z$ forms in single phase and superconducts ($T_{c,0} \approx 22$ K), in this series, whereas in the Ba analog $TbBa_2Cu_3O_y$ does not form in single phase and hence does not superconduct and (2) $EuSr_2Cu_{2.85}Re_{0.15}O_z$ is the nonsuperconducting analog of 1-2-3 compounds with O_7 stoichiometry. The one delineating feature of this study is that superconductivity and structural properties are very sensitive to the variation of the R size. Such a behavior has not been observed before in 1-2-3 analog. Consistent with the above findings, the "mixed" compound $Tm_{0.71}Eu_{0.29}Sr_2Cu_{2.85}Re_{0.15}O_z$ has a $T_c \approx 34$ K, higher than that of the individual members. We also have observed similar kinds of strong variation of T_c with R ions in $RSr_2Cu_{2.8}W_{0.2}O_y$ compounds and we believe that such effects may occur in other Sr-based and M -stabilized 1-2-3-phase $RSr_2Cu_{3-x}M_xO_z$ ($M = Al, Fe, Co, Cr, Mo, \text{ etc.}$).³⁻⁷

ACKNOWLEDGMENT

One of the authors (M.M.) would like to thank the University Grant Commission, New Delhi, for providing financial support.

¹M.B. Maple, Y. Dalichaouch, J.M. Ferreria, R.R. Hake, B.W. Lee, J.J. Neumeier, M.S. Torikachvili, K.N. Yang, H. Zhou, R.P. Guertin, and M.V. Kurik, *Physica B* **148**, 155 (1987).

²K. Okai, *Jpn. J. Appl. Phys.* **29**, L2180 (1990).

³S.A. Sunshine, L.F. Schneomeyer, T. Siegrist, D.C. Douglass, J.V. Waszquez, R.J. Cava, E.M. Gyorgy, and D.W. Murphy, *Chem. Mater.* **1**, 331 (1989).

⁴P.R. Slater and C. Greaves, *Physica C* **180**, 299 (1991).

⁵T. Den and T. Kobayashi, *Physica C* **196**, 141 (1992).

⁶Y. Zhao, F. Shi, H.K. Liu, C. Andrikidis, and S.X. Dou, *Physica C* **212**, 451 (1993).

⁷R. Suryanarayanan, M.S.R. Rao, L. Ouhammou, O. Gorochoy, N.

LeNagard, and H. Pankowska, *Mater. Sci. Forum* **130-132**, 485 (1993).

⁸K.N. Yang, B.W. Lee, M.B. Maple, and S.S. Laderman, *Appl. Phys. A* **46**, 229 (1988).

⁹Q. Xiong, Y.Q. Wang, J.W. Chu, Y.Y. Sun, K. Matsuishi, H.H. Feng, P.H. Hor, and C.W. Chu, *Physica C* **198**, 70 (1992).

¹⁰A. Sequiera, H. Rajagopal, M. Murugesan, M.S.R. Rao, L.C. Gupta, R. Pinto, M. Sharon, and R. Vijayaraghavan (private communication).

¹¹G.V. Subba Rao and U.V. Varadaraju, in *Chemistry of High Temperature Superconductors*, edited by C.N.R. Rao (World Scientific, Singapore, 1991).

¹²R.D. Shannon, *Acta Crystallogr. A* **32**, 751 (1976).