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Chemical control of high-T_c superconductivity of the triple-fluorite-layer copper oxide $(\mathrm{Cu,Mo})\mathrm{Sr}_2(\mathrm{Ce},R)_3\mathrm{Cu}_2\mathrm{O}_{11+\delta}$ (R=Y,La–Yb)

M. Karppinen,[1,*] Y. Morita,[1] J. M. Chen,[2] R. S. Liu,[3] and H. Yamauchi[1]
[1]*Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan*
[2]*National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan, Republic of China*
[3]*Department of Chemistry, National Taiwan University, Taipei, Taiwan, Republic of China*

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For the recently synthesized $(\mathrm{Cu}_{0.75}\mathrm{Mo}_{0.25})\mathrm{Sr}_2(\mathrm{Ce}_{0.67}\mathrm{Y}_{0.33})_3\mathrm{Cu}_2\mathrm{O}_{11+\delta}$ or (Cu,Mo)-1232 high-T_c superconductor, the (Ce,Y) site in the triple-fluorite-structured $(\mathrm{Ce}_{0.67}\mathrm{Y}_{0.33})$-$\mathrm{O}_2$-$(\mathrm{Ce}_{0.67}\mathrm{Y}_{0.33})$-$\mathrm{O}_2$-$(\mathrm{Ce}_{0.67}\mathrm{Y}_{0.33})$ block between two adjacent CuO_2 planes is found flexible enough for rare earths (R) from La to Yb to fully substitute for Y. The superconductivity transition temperature, T_c, monotonically increases with decreasing size of the R constituent, from 26 K for La to 53 K for Y. At the same time the average valence of copper as evaluated from Cu L-edge x-ray absorption near-edge structure spectra is found to remain constant at 2.28 (within ±0.01). Since the samples (especially with large Rs) are underdoped, we believe that the smaller-for-larger R-cation substitution shifts holes from the $(\mathrm{Cu,Mo})\mathrm{O}_{1+\delta}$ charge reservoir into the CuO_2 planes to increase T_c. With R=Tb and Pr, the (Cu,Mo)-1232 structure forms but the samples can not be made superconductive. The reason is found at the lower Cu valence value, i.e., 2.18 for R=Tb. Moreover, the lattice parameters, a and c, for both the R=Tb and Pr samples are significantly shorter than those expected through interpolation of data for the samples with other R constituents. Hence, we suggest that both Tb and Pr in (Cu,Mo)-1232 possess a valence state higher than III.

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For the known high-T_c superconductive copper-oxide phases having rare earth (R) elements as constituents a common feature has been that any of the R elements can be fully substituted by most of other R elements. Tuning the size of R provides us with a means to control the superconductivity characteristics, viz., the "chemical pressure" effect. For the prototype high-T_c superconductor, $\mathrm{CuBa}_2R\mathrm{Cu}_2\mathrm{O}_{7-\delta}$ [i.e., Cu-$1^{(\mathrm{Ba})}2^{(R)}12$ (Ref. 1) or "R-123"] increasing the size of the R constituent decreases T_c,[2] whereas the opposite is true for the other well-known R-based system, $\mathrm{Cu}_2\mathrm{Ba}_2R\mathrm{Cu}_2\mathrm{O}_8$ [Cu-$2^{(\mathrm{Ba})}2^{(R)}12$ (Ref. 1) or "R-124"].[3] Substitution studies involving R elements soon revealed another interesting issue: among the fifteen rare earths (= Sc, Y, La-Lu; omitting radioactive Pm) not only the smallest end members, Sc and Lu, but also Ce, Pr and Tb often behave anomalously.[4,5] Recently we synthesized an R-based $(\mathrm{Cu}_{0.75}\mathrm{Mo}_{0.25})\mathrm{Sr}_2(\mathrm{Ce}_{0.67}\mathrm{Y}_{0.33})_3\mathrm{Cu}_2\mathrm{O}_{11+\delta}$ high-T_c superconductor of the (Cu,Mo)-$1^{(\mathrm{Sr})}2^{(\mathrm{Ce,Y})}32$ phase in which the two adjacent CuO_2 planes are separated by a fluorite-structured (Ce,Y)-O_2-(Ce,Y)-O_2-(Ce,Y) block three (Ce,Y) cation layers thick (with expected valence states of $\mathrm{Ce}^{\mathrm{IV}}$ and $\mathrm{Y}^{\mathrm{III}}$).[6] Here this triple-fluorite-layer superconductor is utilized as an alternate model system for searching for answers to the yet-puzzling questions concerning the anomalously behaving Pr and Tb and the effects of chemical pressure in multilayered copper oxides.

Samples of $(\mathrm{Cu}_{0.75}\mathrm{Mo}_{0.25})\mathrm{Sr}_2(\mathrm{Ce}_{0.67}R_{0.33})_3\mathrm{Cu}_2\mathrm{O}_{11+\delta}$ with R=La, Pr, Nd, Eu, Gd, Tb, Dy, Y, Ho, and Yb were synthesized by solid-state reaction from appropriate mixtures of high-purity powders of CuO, MoO_3, SrCO_3, CeO_2, $R_2\mathrm{O}_3$ (R=La, Nd, Eu, Gd, Dy, Y, Ho, and Yb), $\mathrm{Tb}_4\mathrm{O}_7$, and $\mathrm{Pr}_6\mathrm{O}_{11}$. The mixed powder was calcined at 950 °C and sintered at 1020 °C in air, except for R=Yb at 1090 °C in flowing O_2 gas with several intermediate grindings. Here it should be noted that we also attempted to synthesize the R=Lu phase, but the phase did not form. To make the as-synthesized (AS) samples superconductive, a subsequent annealing at high oxygen pressures is required.[6] Portions of the AS samples were therefore high-pressure oxygenated (HPO) at 5 GPa and 500 °C for 30 min in a cubic-anvil-type high-pressure apparatus in the presence of $\mathrm{Ag}_2\mathrm{O}_2$ as an excess-oxygen source. The amount of $\mathrm{Ag}_2\mathrm{O}_2$ mixed with the $(\mathrm{Cu}_{0.75}\mathrm{Mo}_{0.25})\mathrm{Sr}_2(\mathrm{Ce}_{0.67}R_{0.33})_3\mathrm{Cu}_2\mathrm{O}_{11+\delta}$ powder was systematically varied from 12.5 to 100 mol % to find out the appropriate amount required to reach the maximum oxygen content for the (Cu,Mo)-$1^{(\mathrm{Sr})}2^{(\mathrm{Ce},R)}32$ phase. All the AS and HPO samples were found to be of single phase within the detection limit of powder x-ray diffraction (XRD) measurement. Lattice-parameter refinement was readily carried out in tetragonal space group, $P4/mmm$, expected for a 1232-type structure. The samples were also characterized for the superconductivity transition temperature, T_c (defined at the onset of the diamagnetic signal in the field-cooling curve recorded at 10 Oe), using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design: MPMS-XL), and for the average (over the two different Cu lattice sites) valence of copper, V(Cu), on the basis of Cu $L_{2,3}$-edge x-ray absorption near-edge structure (XANES) spectroscopy. The XANES spectra were collected at room temperature for selected R-constituent samples in x-ray fluorescence-yield mode at the "6-m HSGM" beam line of the NSRRC in Hsinchu, Taiwan; experimental details were as previously given elsewhere.[7] The spectral features were analyzed following Ref. 7. The intensities of the main peak seen in the Cu L_3-edge area around ~931.2 eV and its high-energy shoulder at ~932.7 eV were fitted with Gaussian functions after ap-

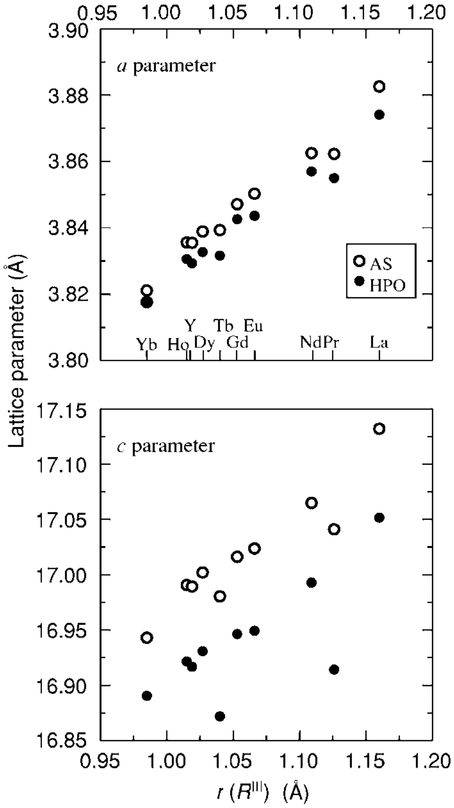

FIG. 1. Lattice parameters, a and c, plotted against the ionic radius, $r(R^{\mathrm{III}})$, of the R constituent (in trivalent state) for both as-synthesized (AS) and high-pressure oxygenated (HPO) samples of $(\mathrm{Cu}_{0.75}\mathrm{Mo}_{0.25})\mathrm{Sr}_2(\mathrm{Ce}_{0.67}\mathrm{R}_{0.33})_3\mathrm{Cu}_2\mathrm{O}_{11+\delta}$.

proximating the background to a straight line. The intensity of the main peak is proportional to the amount of divalent copper $[I(\mathrm{Cu}^{\mathrm{II}})]$, whereas that of the shoulder reflects the amount of trivalent copper $[I(\mathrm{Cu}^{\mathrm{III}})]$. Thus, V(Cu) was estimated by: $V(\mathrm{Cu})=2+I(\mathrm{Cu}^{\mathrm{III}})/[I(\mathrm{Cu}^{\mathrm{II}})+I(\mathrm{Cu}^{\mathrm{III}})]$. Since we did not correct the XANES data for the self-absorption effect,[8] the resultant absolute values for V(Cu) may somewhat (±0.03) deviate from the true Cu valence values. Nevertheless, within the sample series studied, our V(Cu) values should be highly reliable in terms of detecting relative changes or differences in the (average) valence state of copper.

First we investigated the influence of the amount of $\mathrm{Ag}_2\mathrm{O}_2$ used as the excess-oxygen source in the HPO treatments. It was found—for all the R constituents—that with increasing amount of $\mathrm{Ag}_2\mathrm{O}_2$ the lattice parameters decreased and the values of V(Cu) and T_c increased only up to 50–75 mol % of added $\mathrm{Ag}_2\mathrm{O}_2$, and then leveled off. This indicates that the further increase in the amount of $\mathrm{Ag}_2\mathrm{O}_2$ does not increase the oxygen content of the $(\mathrm{Cu}_{0.75}\mathrm{Mo}_{0.25})\mathrm{Sr}_2(\mathrm{Ce}_{0.67}R_{0.33})_3\mathrm{Cu}_2\mathrm{O}_{11+\delta}$ phase. In the following discussion, when referring to HPO samples we mean such "oxygen-saturated" samples.

In Fig. 1 the lattice parameters, a and c, of the tetragonal (Cu,Mo)-$1^{(\mathrm{Sr})}2^{(\mathrm{Ce},R)}32$ unit cell are plotted against $r(R^{\mathrm{III}})$ (=ionic radius[9] of 8-coordinated R in the trivalent state) for the two sample series, AS and HPO. For every R constituent, the HPO treatment results in lattice contraction, as commonly seen for layered copper oxides upon increasing oxygen content. From Fig. 1, magnitude of the lattice-parameter contraction is essentially constant within the entire R substitution range. Hence we conclude that the amount of oxygen incorporated upon HPO treatments is of the same level for all the R constituents. This is consistent with the nearly constant increase in the V(Cu) value revealed from the Cu L-edge XANES spectra for most of the (Cu,Mo)-$1^{(\mathrm{Sr})}2^{(\mathrm{Ce},R)}32$ phases upon HPO treatment (Fig. 2). Moreover, the maximum V(Cu) value itself is apparently constant for most of the HPO samples, which indicates the same absolute oxygen content for these samples.

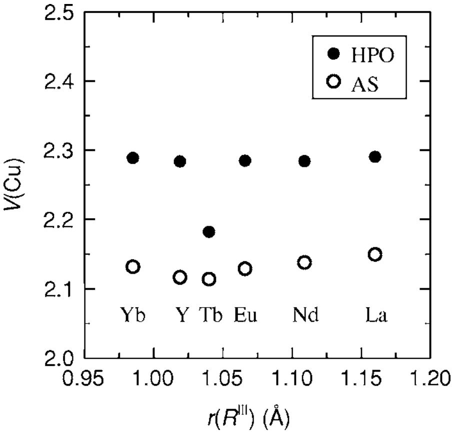

FIG. 2. Average valence of copper, V(Cu), as estimated from Cu L-edge XANES spectra and plotted against the ionic radius, $r(R^{\mathrm{III}})$, of the R constituent (in trivalent state) for selected AS and HPO samples of $(\mathrm{Cu}_{0.75}\mathrm{Mo}_{0.25})\mathrm{Sr}_2(\mathrm{Ce}_{0.67}\mathrm{R}_{0.33})_3\mathrm{Cu}_2\mathrm{O}_{11+\delta}$.

From Fig. 2, among the HPO samples characterized by XANES, V(Cu) remains constant at 2.28±0.01 for all R species except Tb: a significantly lower V(Cu) value of 2.18 is obtained for the sample with R=Tb. It should be noted that for the R=Pr sample, XANES data were collected too, but could not be reliably fitted due to the overlap of Cu L-edge and Pr M-edge spectral features. However, visual comparison was done to conclude that V(Cu) in the R=Pr sample is close to that in the R=Tb sample. Assuming a constant oxygen content (and constant valence values for Mo and Ce) for the entire series of the HPO samples of $(\mathrm{Cu}_{0.75}\mathrm{Mo}_{0.25})\mathrm{Sr}_2(\mathrm{Ce}_{0.67}R_{0.33})_3\mathrm{Cu}_2\mathrm{O}_{11+\delta}$, we calculated from the V(Cu) values that the R valence, $V(R)$, is larger by 0.28 for the R=Tb sample than for those with the rest of R constituents (excluding Pr). Moreover it is revealed from Fig. 2 that among the AS samples too, the R=Tb sample exhibits the lowest V(Cu) value, and hence it is most likely that the V(Tb) value is slightly higher than III. The deviation of V(Cu) for the R=Tb AS sample from those for the rest of AS samples is, however, less pronounced than the one seen for the HPO samples. Notably, we end up with a highly parallel conclusion by analyzing the lattice parameter data of Fig. 1: for all R constituents except Tb and Pr a perfectly linear dependence ("lanthanide contraction") of a and c on $r(R^{\mathrm{III}})$ is apparent for both the sample series, AS and HPO. Taking an analogy to the case of R=Pr[10] in the

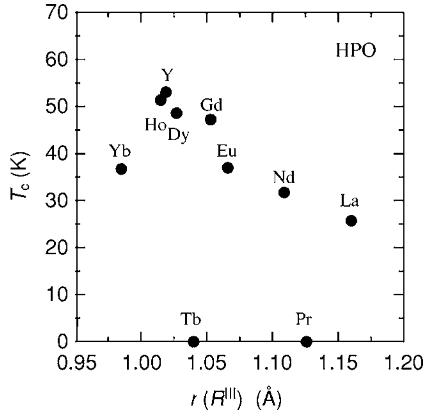

FIG. 3. T_c values for similarly high-pressure oxygenated $(Cu_{0.75}Mo_{0.25})Sr_2(Ce_{0.67}R_{0.33})_3Cu_2O_{11+\delta}$ samples of the (Cu,Mo) $-1^{(Sr)}2^{(Ce,R)}32$ phase plotted against the ionic radius, $r(R^{\rm III})$, of the R constituent (in trivalent state).

Cu-$1^{(Ba)}2^{(R)}12$ system,[2] the shorter-than-expected lattice parameters for the present R=Pr and Tb samples may be considered as an indication of Pr/Tb adapting a valence state higher than III, and a rough estimation for the valence states of Tb and Pr in the AS and HPO samples is obtained from the c parameter data [using tabulated $r(R^{\rm III})$ and $r(R^{\rm IV})$ values[9]] as follows: $V({\rm Tb})_{\rm AS}=3.25$, $V({\rm Tb})_{\rm HPO}=3.51$, $V({\rm Pr})_{\rm AS}=3.21$, $V({\rm Pr})_{\rm AS}=3.45$. Hence, from the point of crystallography, it looks that both Tb and Pr in (Cu,Mo) $-1^{(Sr)}2^{(Ce,R)}32$ possess an intermediate III/IV valence state, not only in the HPO samples but (to a lesser extent) even in the lower-oxygen-content AS samples. Here it is interesting to refer again to the Cu-$1^{(Ba)}2^{(R)}12$ system in which crystallographic data indicated a valence value greater than III for Pr only in the oxygen-rich $CuBa_2RCu_2O_7$ phase, whereas among the oxygen-depleted samples of $CuBa_2RCu_2O_6$ the R=Pr phase perfectly followed the general lanthanide-contraction behavior.[2,10]

In Fig. 3, the value of T_c is plotted against $r(R^{\rm III})$ for the HPO samples. All the HPO samples (except those with R =Tb and Pr) show superconductivity with the T_c values ranging from 23 K for R=La to 53 K for R=Y. The absence of superconductivity in the R=Tb and Pr samples is well justified from the lower valence state of copper in these samples. Rather, in Fig. 3 we should pay attention to another interesting feature: for the superconductive (Cu,Mo)-$1^{(Sr)}2^{(Ce,R)}32$ samples T_c increases almost linearly with decreasing $r(R^{\rm III})$ down to $r({\rm Ho}^{\rm III})$. At the same time the XANES data confirmed that among the superconductive samples the average valence of copper remains constant within the entire $r(R^{\rm III})$ range. This suggests that the size of the R constituent affects the charge distribution between the $(Cu,Mo)O_{1+\delta}$ charge reservoir and the superconductive CuO_2 planes. Unfortunately, Cu L-edge XANES spectroscopy does not allow us to distinguish valence values of the two crystallographically distinct Cu atoms in (Cu,Mo)-$1^{(Sr)}2^{(Ce,R)}32$. To find an explanation for the presently observed T_c vs $r(R^{\rm III})$ dependence, we again consider the Cu-$1^{(Ba)}2^{(R)}12$ and Cu-$2^{(Ba)}2^{(R)}12$ systems in which the effects of wide-range R-cation replacements have already been established. (1) For Cu-$1^{(Ba)}2^{(R)}12$ $(CuBa_2RCu_2O_{7-\delta})$ the isovalent smaller-for-larger $R^{\rm III}$ substitution is believed [based on the Seebeck coefficient,[11] O K-edge XANES (Ref. 12) and bond-valence-sum[13,14] data] to result in a shift of holes from the $CuO_{1-\delta}$ charge reservoir to the superconductive CuO_2 plane when the size of the R constituent between two adjacent CuO_2 planes is decreased. Since fully oxygenated samples of the Cu-$1^{(Ba)}2^{(R)}12$ phase are in a slightly overdoped state, such an increase in the CuO_2-plane hole concentration decreases the T_c value[2,14] as it makes the phase more heavily overdoped. (2) The Cu $-2^{(Ba)}2^{(R)}12$ $(Cu_2Ba_2RCu_2O_8)$ superconductors, on the other hand, are known to be underdoped (unless $R^{\rm III}$ is partly substituted by divalent calcium), explaining why T_c rather increases[3] with shifting holes from the $(CuO)_2$ charge reservoir to the CuO_2 planes as $r(R^{\rm III})$ decreases in this system. Now, assuming that for the present (Cu,Mo)-$1^{(Sr)}2^{(Ce,R)}32$ system too, holes are gradually shifted from the $(Cu,Mo)O_{1+\delta}$ charge reservoir to the CuO_2 planes with decreasing $r({\rm R}^{\rm III})$, one reaches the conclusion that the present $(Cu_{0.75}Mo_{0.25})Sr_2(Ce_{0.67}R_{0.33})_3Cu_2O_{11+\delta}$ samples are underdoped. This is actually what one may also conclude from the fact that upon loading these samples with an increasing amount of oxygen, T_c monotonically increases (up to the very level of "oxygen saturation" reached with the present HPO technique).[6] Finally we should comment on the anomalously low T_c value of the R=Yb sample (Fig. 3). Since the average Cu valence for this sample is just the same as that for the other superconductive (Cu,Mo)-$1^{(Sr)}2^{(Ce,R)}32$ samples (Fig. 2), one of the following explanations may stand: (1) the shift of holes from the $(Cu,Mo)O_{1+\delta}$ charge reservoir to the CuO_2 planes has made the sample come into the overdoping region in the case of R=Yb, or (2) some (not yet addressed) lattice-mismatch effect becomes severe enough to depress the T_c. It should be recalled that to obtain the R=Yb sample required were synthesis conditions a little different from those for the samples with other R constituents.

In conclusion, we have arrived at a model system that provides us with an opportunity to extend the yet-limited understanding upon the effects of chemical pressure and the behaviors of the puzzlingly behaving rare earths, Tb and Pr, in high-T_c superconductive layered copper oxides. In the rather exotic (Cu,Mo)-1232 system presented here, the (Ce,Y) site in the triple-fluorite-layer block between the two adjacent CuO_2 planes was found flexible enough to be occupied by R elements ranging (in terms of size) from La down to Yb. For samples that possessed the same average Cu valence value, the value of T_c was found to increase with decreasing size of the R constituent. The following interpretation was proposed for this: The samples with the largest R constituents are clearly underdoped but the smaller-for-larger R-cation substitution promotes shift of holes from the $(Cu,Mo)O_{1+\delta}$ charge reservoir to the superconductive CuO_2

planes such that the hole-doping level of the CuO_2 planes may approach the optimum level to raise the value of T_c towards the maximum value. Moreover, it was found that unlike the samples with the rest of R constituents, the R =Tb and Pr samples remained nonsuperconductive possessing a Cu valence value significantly lower than those of other similarly treated samples. This suggested that Tb and Pr in the samples possess valence values higher than III.

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*Corresponding author. Electronic address: karppinen@msl.titech.ac.jp

[1] M. Karppinen and H. Yamauchi, Mater. Sci. Eng., R. **26**, 51 (1999).

[2] M. Guillaume, P. Allenspach, W. Henggeler, J. Mesot, B. Roessli, U. Staub, P. Fischer, A. Furrer, and V. Trounov, J. Phys.: Condens. Matter **6**, 7963 (1994).

[3] D. E. Morris, J. H. Nickel, J. Y. T. Wei, N. G. Asmar, J. S. Scott, U. M. Scheven, C. T. Hultgren, A. G. Markelz, J. E. Post, P. J. Heaney, D. R. Veblen, and R. M. Hazen, Phys. Rev. B **39**, 7347 (1989).

[4] L. Soderholm, K. Zhang, D. G. Hinks, M. A. Beno, J. D. Jorgensen, C. U. Segre, and I. K. Schuller, Nature (London) **328**, 604 (1987).

[5] E. Hodorowicz, S. A. Hodorowicz, and H. A. Elick, J. Alloys Compd. **181**, 442 (1992); H. B. Radousky, J. Mater. Res. **7**, 1917 (1992); M. Akhavan, Physica B **321**, 265 (2002), and references therein.

[6] Y. Morita, T. Nagai, Y. Matsui, H. Yamauchi, and M. Karppinen, Phys. Rev. B **70**, 174515 (2004).

[7] M. Karppinen, M. Kotiranta, T. Nakane, H. Yamauchi, S. C. Chang, R. S. Liu, and J. M. Chen, Phys. Rev. B **67**, 134522 (2003).

[8] It was considered counterproductive to carry out self-absorption correction due to not-well-defined amounts of Ag and Ag_2O in the samples.

[9] R. D. Shannon, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **32**, 751 (1976).

[10] For Cu-$1^{(Ba)}2^{(R)}$12 the pure R=Tb phase does not form due to the high stability of the competing $BaTbO_3$ phase.

[11] W. N. Kang and M.-Y. Choi, Phys. Rev. B **42**, 2573 (1990).

[12] J. M. Chen, S. J. Liu, C. F. Chang, J.-Y. Lin, Y. S. Gou, and H. D. Yang, Phys. Rev. B **67**, 014502 (2003).

[13] S. V. Samoylenkov, O. Yu Gorbenko, and A. R. Kaul, Physica C **278**, 49 (1997).

[14] Y. Yasukawa, T. Nakane, H. Yamauchi, and M. Karppinen, Appl. Phys. Lett. **78**, 2917 (2001); M. Karppinen, N. Kiryakov, Y. Yasukawa, T. Nakane, and H. Yamauchi, Physica C **382**, 66 (2002).