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1997 J. Phys.: Condens. Matter 9 L75

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## LETTER TO THE EDITOR

**Anomalies in thermoelectric power at 200 K in the calcium-doped NdCeCuO system**

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Received 16 October 1996

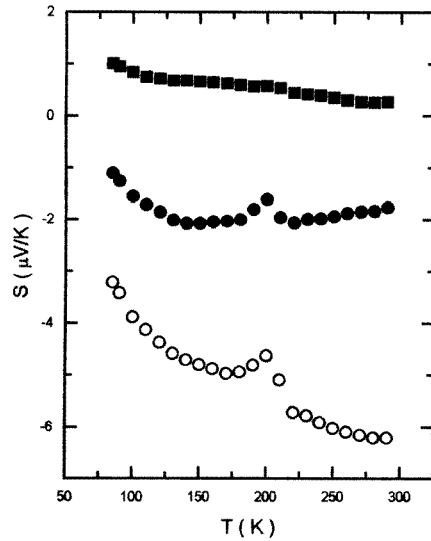
**Abstract.** Samples of  $\text{Nd}_{1.85-x}\text{Ce}_{0.15}\text{Ca}_x\text{CuO}_y$  are characterized by thermoelectric power and variable-temperature x-ray diffraction. For the superconducting sample  $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_y$ ,  $S$  is positive in the whole measuring temperature range and weakly dependent on temperature; for the Ca-doped samples,  $\text{Nd}_{1.85-x}\text{Ce}_{0.15}\text{Ca}_x\text{CuO}_y$ ,  $S$  shows a negative and strong dependence on temperature at low temperature for large  $x$ . It is striking that Ca doping leads to a sharp peak at about 200 K for either the superconducting samples  $\text{Nd}_{1.85-x}\text{Ce}_{0.15}\text{Ca}_x\text{CuO}_y$  or the nonsuperconducting samples  $\text{Nd}_{2-x}\text{Ca}_x\text{CuO}_y$ . The strength of the peak increases with increasing  $x$ . Low-temperature x-ray diffraction shows that the lattice parameters decrease with decreasing temperature and an anomaly is observed at the corresponding temperature.

The discovery of the electron-doped high- $T_c$  superconductors  $\text{R}_{2-x}\text{Ce}_x\text{CuO}_{4+\delta}$  (where R is Nd, Pr, or Sm) has stimulated intensive studies on the transport properties and spin magnetism in this system since initial observations of negative thermoelectric power (TEP) and Hall coefficient in  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  (NCCO) appear to confirm that Ce contributes electron-like carriers to the  $\text{CuO}_2$  planes [1], as expected for  $\text{Ce}^{4+}$  substituting for  $\text{Nd}^{3+}$ . This provides evidence that the  $\text{CuO}_2$  planes display a symmetry with respect to electron or hole doping. A controversial problem in superconductivity has been the nature of the charge carriers in electron-doped cuprates. Recent many reports of a positive Hall effect and TEP suggest that the dominant carriers are positively charged [2, 3]. In particular, Jiang *et al* [4] study transport properties of the NCCO system and observe a gradual change of Hall coefficient from negative to positive on the removal of oxygen. TEP is an important transport coefficient complementary to the electrical resistivity and Hall effect and can probe the charge carrier properties and carrier–phonon interactions. On the other hand, it is well known that the TEP ( $S$ ) is often less affected by sample imperfections. Measurements of  $S(T)$  are equally valid on sintered samples as the TEP of untextured polycrystalline samples is just the  $a$ – $b$  plane TEP [5]. Many results for the TEP of  $\text{R}_{2-x}\text{Ce}_x\text{CuO}_{4+\delta}$  (R = Nd, Pr, Sm) have been reported [1, 3, 6–8]. Nevertheless, as concerns the intrinsic sign of the TEP, the reports differ. In order to understand the nature of the charge carrier in the NCCO system, we recently investigated the transport properties (resistivity and Hall coefficient) for the samples NdCeCaCuO with coexistence of electron- and holelike carriers by doping  $\text{Ca}^{2+}$  and  $\text{Ce}^{4+}$  in  $\text{Nd}_2\text{CuO}_{4+\delta}$  [9]. Here we report the measurements of TEP for the same samples used in measuring Hall effect and resistivity to investigate changes in the

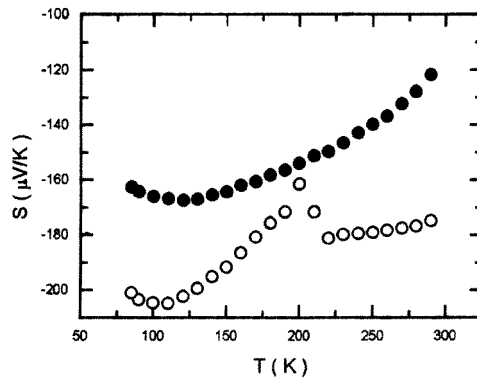
charge-carrier density and electronic structure due to Ca doping, and the structure change observed by variable-temperature (77–300 K) x-ray diffraction for the same sample as used in measuring the Hall effect and resistivity. It is found that the TEP of the superconducting Ca-free material (NdCeCuO) is positive and small and that Ca doping leads to a sign change in TEP (that is, negative for Ca-doped samples) and a sharp peak appearing in  $S(T)$  at about 200 K. At the corresponding temperature, a structural anomaly is also observed by variable-temperature x-ray diffraction and a turning point exists in the lattice parameters' dependence on temperature.

Samples of nominal composition  $\text{Nd}_{1.85-x}\text{Ce}_{0.15}\text{Ca}_x\text{CuO}_{4-\delta}$  were prepared by two steps in order to obtain samples with a single phase. The precursor was prepared by thoroughly mixing high-purity powders of  $\text{Nd}_2\text{O}_3$ ,  $\text{CaCO}_3$  and  $\text{CuO}$  according to the nominal composition  $\text{Nd}_{1.85-x}\text{Ca}_x\text{CuO}_y$  ( $x = 0, 0.1, 0.2, 0.3$ ). The mixture was ground and fired at  $1000^\circ\text{C}$  for 20 h, then reground and refired at  $1100^\circ\text{C}$  for 20 h. The appropriate amount of  $\text{CeO}_2$  was added to the precursor obtained above, and the mixture was ground and fired at  $1050^\circ\text{C}$  for several overnight cycles of calcining and mechanical grinding. The resulting powder was pressed into pellets and sintered at  $1120^\circ\text{C}$  for 20 h, then quenched to room temperature. The preparation procedure of the  $\text{Nd}_{2-x}\text{Ca}_x\text{CuO}_{4+\delta}$  samples ( $x = 0, 0.07, 0.15, 0.25$ ) is similar to that of the precursor. All firing procedures are performed in air. A second annealing at  $950^\circ\text{C}$  under  $\text{N}_2$  is carried out in order to induce superconductivity in these samples. Room-temperature and variable-temperature x-ray diffraction measurements with  $\text{Cu K}\alpha$  radiation are used to determine the range of existence of the solid solution and the lattice parameters' dependence on temperature. Lattice parameters for single-phase materials are refined using the Bragg peaks over the  $\theta$  range. The TEP coefficient was measured by a dc method in the temperature range between 77 and 300 K. The temperature gradient ( $\Delta T$ ) in the sample was measured using the two pairs of copper–constantan thermocouples. The sample was mounted on top of two well separated copper blocks with silver paint. During the measurement the temperature gradient  $\Delta T$  of two separated copper blocks was kept at 2 K. To eliminate the effects of the reference leads, the absolute thermoelectric power of copper was subtracted from the measured thermoelectric voltage. All samples used in TEP and x-ray diffraction measurements are the same as used for the resistivity and Hall effect measurements reported in [9]. In [9], energy dispersive spectrum (EDS) elemental analysis showed that Ca is actually incorporated into the  $(\text{Nd,Ce})_2\text{CuO}_y$  system and that the actual composition is nearly the same as the nominal composition except for a slightly higher concentration of Nd. The sample preparation, solid solution range, and results on resistivity and Hall effect have been reported in detail in [9].

The results for the TEP of the samples  $\text{Nd}_{1.85-x}\text{Ca}_x\text{Ce}_{0.15}\text{CuO}_{4-\delta}$  are plotted in figure 1 in the temperature range from 77 to 300 K. Figure 1 shows that the TEP of the Ca-free sample is positive and small, and is weakly dependent on temperature, while the TEP is negative for the Ca-doped samples. It indicates that Ca doping leads to a change in TEP sign from positive to negative. It is also found that the magnitude of  $|S|$  increases with increasing Ca concentration. This suggests that Ca doping seems to induce a holelike carrier in the NdCeCuO system. In [9], it was reported that Ca doping induces a loss of oxygen so as to make the valence of Cu nearly the same as that in Ca-free materials. The results for the Hall effect also showed that Ca doping seems to induce a holelike carrier in the NdCeCuO system. This is because Ca doping leads to displacement of oxygen to make the energy of the O p band cross the Fermi level and a holelike state is thus introduced into the  $\text{CuO}_2$  plane. Although many studies on the TEP of NdCeCuO show that the intrinsic sign of the TEP is different and the sign of TEP is dependent on the sample, there is a clear trend that the decrease in oxygen content or the increase in Ce concentration drives the



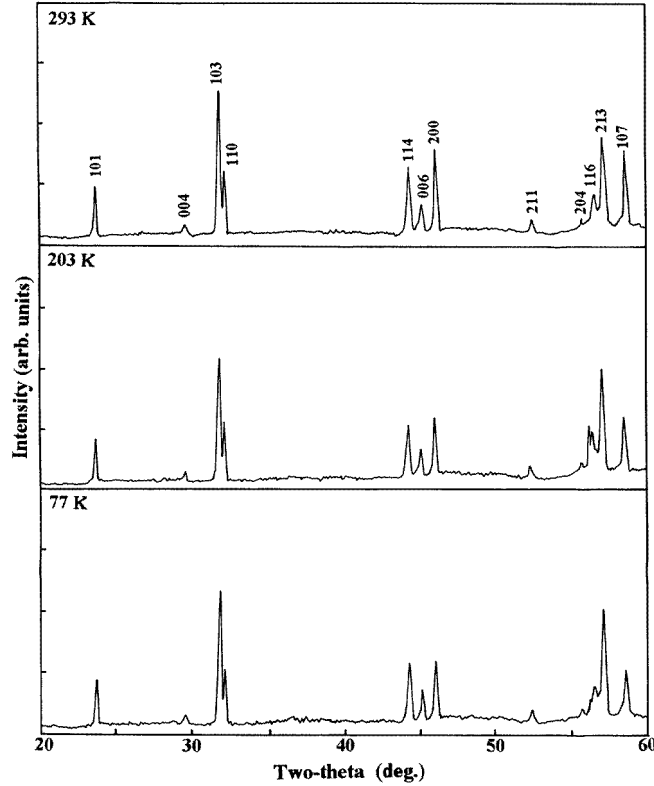
**Figure 1.** The temperature dependence of the TEP for the superconducting samples,  $\text{Nd}_{1.85-x}\text{Ce}_{0.15}\text{Ca}_x\text{CuO}_4$ : ■,  $x = 0$ ; ●,  $x = 0.1$ ; ○,  $x = 0.3$ .



**Figure 2.** The temperature dependence of the TEP for the nonsuperconducting samples,  $\text{Nd}_{2-x}\text{Ca}_x\text{CuO}_{4+\delta}$ : ●,  $x = 0$ ; ○,  $x = 0.15$ .

TEP of NdCeCuO samples (a so-called n-type superconductor) from negative to positive. From a naive picture, reducing oxygen content should have a similar effect as increasing Ce content. Figure 1 shows that the increase in Ca concentration has the opposite effect on thermoelectric power to reducing Ce content, as expected for  $\text{Ca}^{2+}$  substituting for  $\text{Nd}^{3+}$ .

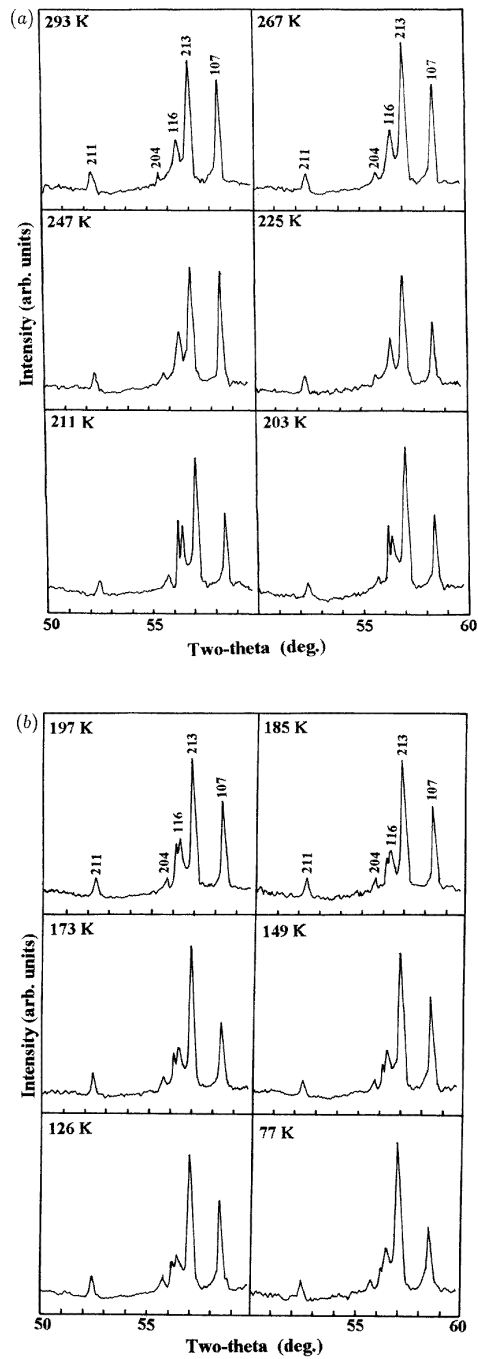
We find positive  $S$ , in apparent conflict with the negative  $R_H$ , for the Ca-free sample; this contradiction is also found for the sample with  $x = 0.3$ . This behaviour has been observed in an NdCeCuO single crystal by Xu *et al* [3]. Thus the simple relation between carrier charge and the sign of the TEP and Hall effect does not hold in the electron-doped superconductor. For the hole-doped cuprates, both  $S$  and  $R_H$  are generally positive below the optimum doping. The change in sign of the room-temperature TEP occurs for hole carrier



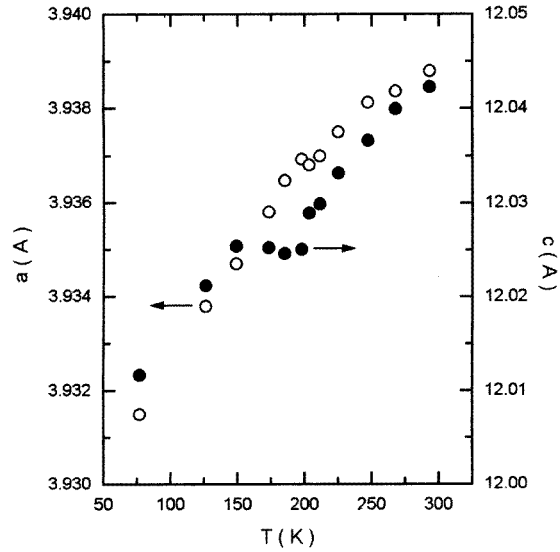
**Figure 3.** The x-ray diffraction patterns for the  $\text{Nd}_{1.75}\text{Ce}_{0.15}\text{Ca}_{0.1}\text{CuO}_4$  sample at different temperatures.

concentrations close to the maximum in  $T_c$  as found for Y-123 [10, 11] and for Tl-1212 and Tl-2201 [5], while for most hole-doped cuprate superconductors the Hall coefficient remains positive in this overdoped region [10, 12].

Figure 2 shows that the large TEP ( $|S| \sim 100\text{--}200 \mu\text{V K}^{-1}$ ) of the nonsuperconducting samples  $\text{Nd}_{2-x}\text{Ca}_x\text{CuO}_{4+\delta}$  is negative over the full temperature range  $T \leq 300$  K. The absolute value of TEP increases with increasing Ca content. This is consistent with the nature of the charge carrier induced by Ca doping into the superconducting  $(\text{Nd, Ce})_2\text{CuO}_4$ . It is also noted that the magnitude of TEP is small for the superconducting samples  $\text{Nd}_{1.85-x}\text{Ca}_x\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ ; the small magnitude of TEP is typical of metals, and the  $T$  dependence is similar for all samples.  $S$  is nearly linear at high temperature, with negative slope  $dS/dT$ , while there is a large magnitude of TEP, the TEP is negative and  $dS/dT$  is positive at high temperature for the nonsuperconducting samples  $\text{Nd}_{2-x}\text{Ca}_x\text{CuO}_{4+\delta}$ . Figure 2 shows a clear upturn in the low-temperature range; the TEP is expected to extrapolate to zero for  $T \rightarrow 0$  as a result of the entropy of the system becoming zero as temperature decreases to zero. For the Ca-free sample  $\text{NdCeCuO}$ ,  $S$  is weakly dependent on temperature and the temperature variation is still essentially linear with a slope  $dS/dT \sim -0.003 \mu\text{V K}^{-2}$ .  $|S|$  of the  $x = 0.1$  sample weakly rises ( $dS/dT \sim 0.001 \mu\text{V K}^{-2}$ ) as the temperature decreases above about 120 K and then reduces steeply ( $dS/dT \sim -0.02 \mu\text{V K}^{-2}$ ), while  $|S|$  of the  $x = 0.3$  sample continuously reduces



**Figure 4.** The series of x-ray diffraction patterns for the  $\text{Nd}_{1.75}\text{Ce}_{0.15}\text{Ca}_{0.1}\text{CuO}_4$  sample in the temperature range between 77 and 300 K.



**Figure 5.** The temperature dependence of the lattice parameters for the  $\text{Nd}_{1.75}\text{Ce}_{0.15}\text{Ca}_{0.1}\text{CuO}_4$  sample.

as temperature decreases, but the slope  $dS/dT \sim -0.01 \mu\text{V K}^{-2}$  above 120 K and  $\sim -0.03 \mu\text{V K}^{-2}$  below 120 K. For the nonsuperconducting samples  $\text{Nd}_{2-x}\text{Ca}_x\text{CuO}_{4+\delta}$ , the slope  $dS/dT$  is positive in the high-temperature region. It seems to be different from that of the superconducting samples. For  $\text{Nd}_2\text{CuO}_{4+\delta}$ , the result is similar to that reported by Sugiyama *et al* [8]. To date, the theory of the TEP has certainly not yet been given in a complete form, but it is generally believed that the negative slope  $dS/dT$  is mainly due to diffusion thermopower (linear in  $T$ ) of the carriers at high temperature, while it is not clear that the absolute value of TEP rapidly reduces with decreasing temperature at low temperature.

It is striking that a sharp peak appears in figures 1 and 2 at about 200 K in both superconducting and nonsuperconducting Ca-doped samples, while no peak is observed for the Ca-free samples. The strength of the peak increases with increasing Ca content. This suggests that the peak is closely related to Ca doping. However, this anomaly is not observed in Hall effect and resistivity measurements. We believe that the anomaly could arise from a structural change induced by Ca doping. It is well known that in the  $T'$  phase Nd(Ca) is located at an eight-coordinated site and the ionic radii of eight-coordinated  $\text{Nd}^{3+}$  and  $\text{Ca}^{2+}$  are 1.25 and 1.26 Å, respectively. Thus, based only on the ionic radius, Ca substitution for Nd should not produce any structure change. However, the  $T'$  phase contains fluorite-type oxygen sandwiched between the rare earth layers, and fluorite-type oxides are prone to oxygen defects. In particular,  $\text{Ca}^{2+}$  occupation in the rare earth ( $\text{Ln}^{3+}$ ) layers leads to a decrease in oxygen coordination and oxygen displacement due to electric charge balance. This could cause a structural change (such as oxygen ordering or oxygen displacement); notably rare earth metal (Nd, Pr, Sm) substituted by  $\text{Sr}^{2+}$  results in a disproportionation into p-type T phase and undoped  $T'$  phase due to lattice mismatch [13].

In order to understand the anomaly in TEP, variable-temperature x-ray diffraction is carried out. Figure 3 shows the x-ray powder diffraction patterns at different temperatures for the  $\text{Nd}_{1.75}\text{Ce}_{0.15}\text{Ca}_{0.1}\text{CuO}_{4-\delta}$  sample. The room-temperature x-ray diffraction pattern

indicates that the sample is a single phase which can be indexed by the  $T'$  phase with  $a = 3.939 \text{ \AA}$  and  $c = 12.043 \text{ \AA}$ . The data from figure 3 indicate that the pattern at different temperatures is nearly the same except that the (116) peak begins to be split into two peaks at about 200 K, the temperature at which the anomaly in TEP is observed. At 77 K the strength of the split peak becomes very weak. In order to observe the (116) peak splitting in detail, figure 4 shows the series of x-ray diffraction patterns in the two-theta range from  $5$  to  $60^\circ$  at different temperatures between room temperature and 77 K. It is found that the pattern remains unchanged until the temperature of 211 K. At 211 K, the (116) peak is split into the two strong peaks. The strength of the left peak reduces with decreasing temperature. The temperature at which the (116) peak splits into two peaks is coincident with that of the TEP anomaly. This suggests that the anomaly in TEP could arise from a structural change. The lattice parameters' dependence on temperature is shown in figure 5. Figure 5 indicates that the lattice parameters decrease with decreasing temperature. It is also found that there exists a turning point at 200 K for the  $a$  axis: the slope above 200 K is different from that below 200 K, while a flat step appears in the temperature range between 200 and 150 K for the  $c$  axis. This suggests that change of the structure takes place at about 200 K. So far, it is difficult to say that the change is a structural phase transition since a similar anomaly is not observed in the resistivity and Hall effect in addition to no anomalous peak appearing in the specific heat measurements. On the other hand, the TEP of sintered samples closely resembles the  $ab$  plane TEP of single crystals [14, 15] and is much less sensitive to the porosity than the resistivity, and heat current is more efficiently transported through grain boundaries or other weak links than electric current. Neutron- and x-ray diffraction analyses indicated that there were no structural phase transitions in the temperature range between 320 and 4.2 K in  $\text{Nd}_2\text{CuO}_4$  and  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  [16]. This is consistent with no anomaly being found in our TEP measurements for  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  ( $x = 0, 0.15$ ) without Ca. Therefore, the preparation of a single crystal is necessary to confirm whether a structural phase transition exists for the Ca-doped NdCeCuO system. It is not clear why Ca doping leads to a structural change at about 200 K. It is well known that the bond-length match between Cu–O and Ln–O bonds is important for the remaining  $T'$  phase.  $\text{Sr}^{2+}$  cannot be doped into  $(\text{Nd}, \text{Ce})_2\text{CuO}_4$  since the ionic radius of  $\text{Sr}^{2+}$  is large. Although the ionic radius of  $\text{Ca}^{2+}$  is nearly the same as that of  $\text{Nd}^{3+}$ , which is the reason that Ca doping into the  $T'$  phase can be achieved, their valences are different. Therefore, it results in a decrease in coordination number around Nd(Ca) sites and oxygen displacement. This displacement transforms the  $\text{O}_2$  layer into the oxygen defect Ln layers and causes structural change. A single crystal is needed to investigate the structural change.

In summary, the superconducting  $\text{Nd}_{2-x}\text{Ce}_{0.15}\text{Ca}_x\text{CuO}_4$  samples and nonsuperconducting  $\text{Nd}_{2-x}\text{Ca}_x\text{CuO}_4$  samples have been studied by TEP and variable-temperature x-ray diffraction. The TEP of the superconducting NdCeCuO is small and positive and weakly dependent on temperature in the temperature range between 77 and 300 K. However, in Ca-doped samples,  $S$  is negative with  $dS/dT < 0$  in the measured temperature range; the absolute value of TEP increases with increasing Ca. For the nonsuperconducting samples,  $S$  is negative and large. Ca doping leads to an increase in the absolute value of TEP. These results suggest that Ca doping changes the nature of the charge carrier and seems to induce a holelike carrier in the  $T'$  phase. There exists an apparent sign conflict between TEP and Hall effect for the superconducting samples. It is striking that an anomalous peak is observed in the TEP at about 200 K. The variable-temperature x-ray diffraction shows a structural change at the corresponding temperature. The lattice parameters decrease with decreasing temperature, but there exists a turning point for the  $a$  axis and a flat step for the  $c$  axis at about 200 K. Study on a single crystal is necessary to further understand the



structural change and the TEP anomaly, especially to measure the resistivity and Hall effect of a single crystal to confirm whether there exists in this case also anomalous behaviour.

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