

## THERMOELECTRIC POWER OF $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ AND $\text{YBa}_2\text{Cu}_4\text{O}_8$ UNDER PRESSURE

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Thermoelectric power (TEP) of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (123) and  $\text{YBa}_2\text{Cu}_4\text{O}_8$  (124) samples are measured as a function of pressure. The TEP of an as-sintered 123 polycrystalline sample shows a broad maximum around 1.25 GPa whereas that of the cold-pressed sample decreases steadily. The ab-plane TEP of 123 single crystal decreases monotonically and the c-axis TEP exhibits a maximum around 1.5 GPa. Disappearance of the broad maximum in the polycrystalline sample upon cold-pressing is interpreted in terms of the crystallite orientation occurring under pressure. TEP of the 124 polycrystalline sample decreases sharply up to 4.5 GPa and at a lower rate with further increase in pressure, a trend similar to that is observed in the variation of  $T_c$  as a function of pressure.

### INTRODUCTION

Much emphasis is being placed on the normal-state properties of high  $T_c$  superconductors, as an understanding of the mechanism of conduction in this state is likely to provide an insight into the mechanism of superconductivity. Ambient pressure thermoelectric power (TEP)<sup>1-5</sup>, resistivity<sup>5,6</sup> and thermal conductivity<sup>7</sup> measurements on single crystals indicate that these systems are highly anisotropic. High-pressure studies have been mostly confined to the measurement of  $T_c$ <sup>8-11</sup> and compressibility<sup>12,13</sup> as a function of pressure. In this paper, the effect of pressure on the TEP of both polycrystalline and single-crystal  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (123) and polycrystalline  $\text{YBa}_2\text{Cu}_4\text{O}_8$  (124) in the normal state are reported. Site descriptions for copper and oxygen are as follows: the chain oxygen is O(4), apical oxygen is O(1) and the plane oxygens are O(2) and O(3). Chain copper is designated Cu(1) and the plane copper Cu(2).

### EXPERIMENTAL DETAILS

Polycrystalline 123 and 124 compounds were synthesised by standard solid-state techniques. Phase purity of the samples was checked from x-ray diffraction patterns. Oxygen content in the 123 samples was estimated by iodimetric titration. The 123 single crystals were grown by the procedure reported earlier<sup>14</sup>.

A tungsten carbide-opposed anvil setup with 12.5 mm anvil face was used in the TEP measurements as a function of pressure. Talc was used as a pressure

transmitting medium. A sample piece (a piece from the sintered pellet in the case of polycrystalline sample) measuring approximately 4 mm × 1 mm and 0.3 mm thick was set in a pyrophyllite gasket (all the gaskets used in the measurements were with i.d. of 5 mm and o.d. of 12.5 mm) with a mixture of talc and epoxy. The epoxy was allowed to set and the gasket-sample assembly was thinned down to 0.27 mm by working both sides of the assembly on a 600 grade emery paper. A stack of three gaskets was used in the measurements. The lower gasket (0.4 mm thick) with a talc disk (also 0.4 mm thick) at the center contained the two thermojunctions (chromel-alumel) and an insulated heater wire spaced 1 mm from each other. The gasket-sample assembly was placed on top of the lower gasket such that the sample was in contact with the thermojunctions and the heater wire. The third gasket (0.2 mm thick) with a talc disc at the center insulated the sample from the top anvil. Temperature gradient across the sample was established by passing suitable current through the heater wire. TEP was calculated by measuring the voltage drop across the two chromel wires and the two alumel wires<sup>15</sup>. For measuring TEP along the c-axis of the 123 single crystal, one thermojunction was placed on the lower gasket and the other on the top gasket. The two gaskets were of the same thickness (0.3 mm). The heater wire was wound on the lower anvil. Details of the set-up are given elsewhere<sup>16</sup>.

## RESULTS AND DISCUSSION

### *123 Samples*

The values of  $x$  as determined from the iodimetric titration in the two polycrystalline samples were 0.17 and 0.21, with  $T_c$ 's of 94.5 and 88.5. The pressure dependence of TEP for the two samples is shown in fig. 1. The TEP of as prepared sample with  $x = 0.17$  increases from a value of  $4 \mu\text{VK}^{-1}$  at ambient pressure to a maximum of  $9 \mu\text{VK}^{-1}$  around 1.25 GPa after which TEP decreases monotonically with further increase in pressure. Thus, the TEP of the as-prepared sample exhibits a shallow maximum between 1 and 1.5 GPa. The TEP of the cold-pressed sample (to above 1.5 GPa) decreases steadily without showing any maximum. The TEP of the cold-pressed sample with  $x = 0.21$  also has the same behavior as a function of pressure as that of the sample with  $x = 0.17$  except for the higher TEP value.

The  $S_{ab}$  (TEP along ab-plane) of single crystal 123 as a function of pressure is shown in fig. 2. TEP has a value of  $10.5 \mu\text{VK}^{-1}$  at ambient pressure and decreases monotonically reaching a value of  $2.5 \mu\text{VK}^{-1}$  at 8 GPa. The c-axis TEP  $S_c$ , also shown in fig. 2, increases initially, reaching a maximum between 1 and 1.5 GPa, and decreases at a rate of  $2.26 \mu\text{VK}^{-1} \text{GPa}^{-1}$  with further increase in pressure.

By the comparison of polycrystalline and single-crystal TEP data, the following inferences can be drawn. The TEP behavior as a function of pressure of the cold-pressed polycrystalline sample is similar to that of the ab-plane TEP of the single crystal, whereas the TEP of the as-sintered polycrystalline sample also has a contribution from the c-axis TEP. It is known that application of uniaxial pressure on a polycrystalline 123 sample tends to orient the crystallites with their ab-plane

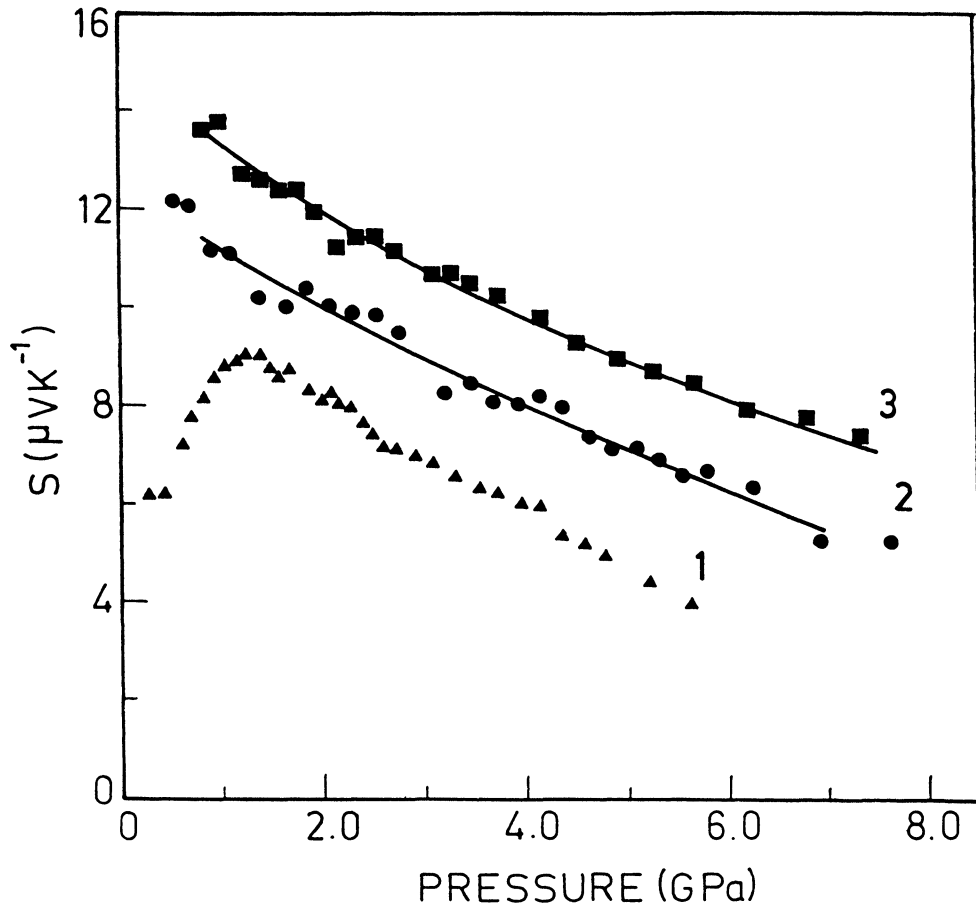


FIGURE 1 TEP vs Pressure of polycrystalline  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  sample: 1. as-sintered with  $x = 0.17$ , 2. same sample after cold-pressing and 3. cold-pressed sample with  $x = 0.21$ .

perpendicular to the direction of the applied load. If indeed the crystallites in the cold-pressed polycrystalline sample are oriented with their *ab*-plane parallel to the anvil face, the TEP behavior in the perpendicular direction should be similar to that of the *c*-axis of the single crystal.

Such TEP measurements were made on the cold-pressed samples and the data are presented in fig. 3. The broad maximum in TEP behavior occurs at a slightly lower pressure. The maximum is not as pronounced as that along the *c*-axis of the single crystal. Magnetic and x-ray diffraction experiments<sup>17</sup> on polycrystalline 123 show that the degree of alignment in the bulk of the pellet was about 1/3 to 1/2 of that on the surface. Even though the samples used in our experiments are less than 0.3 mm thick, it seems that the orientation is not complete throughout the thickness of the sample. Thus, when TEP measurements are made along the thickness of the cold-pressed sample, both aligned and non-aligned portions of the sample contribute to the TEP behavior as a function of pressure.

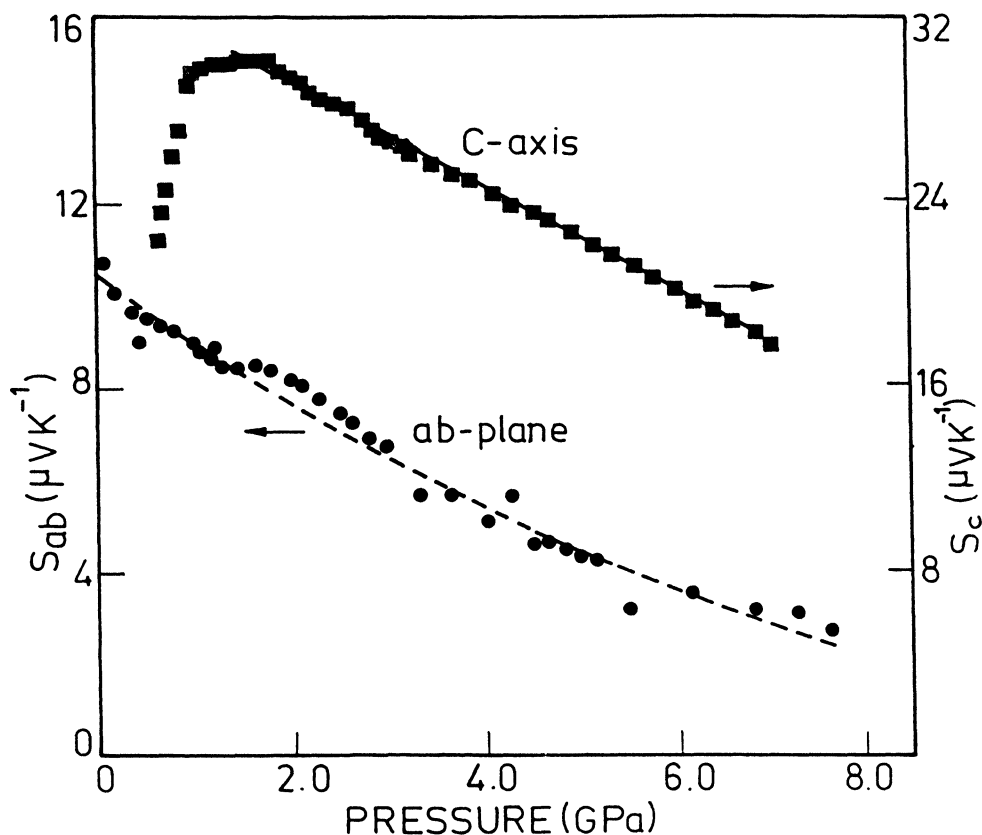


FIGURE 2 TEP vs Pressure data of single crystal  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  both along ab-plane and c-axis.

The ab-plane TEP of the single crystal,  $S_{ab}$ , decreases monotonically with increasing pressure. This behavior can be correlated to the decreasing cell parameters upon application of pressure as seen from x-ray diffraction studies on polycrystalline 123. Thus, bandwidths in the ab-plane would increase, making  $S_{ab}$  more metallic with increasing pressure. However, the variation of  $S_c$  with pressure is quite different. Neutron diffraction studies<sup>18</sup> as a function of pressure show that even though the c-cell parameter decreases with increasing pressure, the Cu(1)-O(1) bond distance remains almost constant and the Cu(2)-O(1) distance decreases steadily. From the resistivity measurements<sup>19</sup> on single crystals along the c-axis under uniaxial pressure, it is found that resistivity decreases rapidly with increasing pressure. These measurements were done at fairly low pressures, neutron diffraction up to 0.6 GPa, and resistivity up to 0.1 GPa. The TEP along the c-axis increases initially at low pressures, indicative of a semiconductor-like behavior: beyond 2 GPa, the metallic behavior sets in, decreasing the TEP with further increase in pressure. Since no data on interplanar distances are available at higher pressures, it is difficult to estimate the critical distances required to induce metal-like behavior along the c-axis.

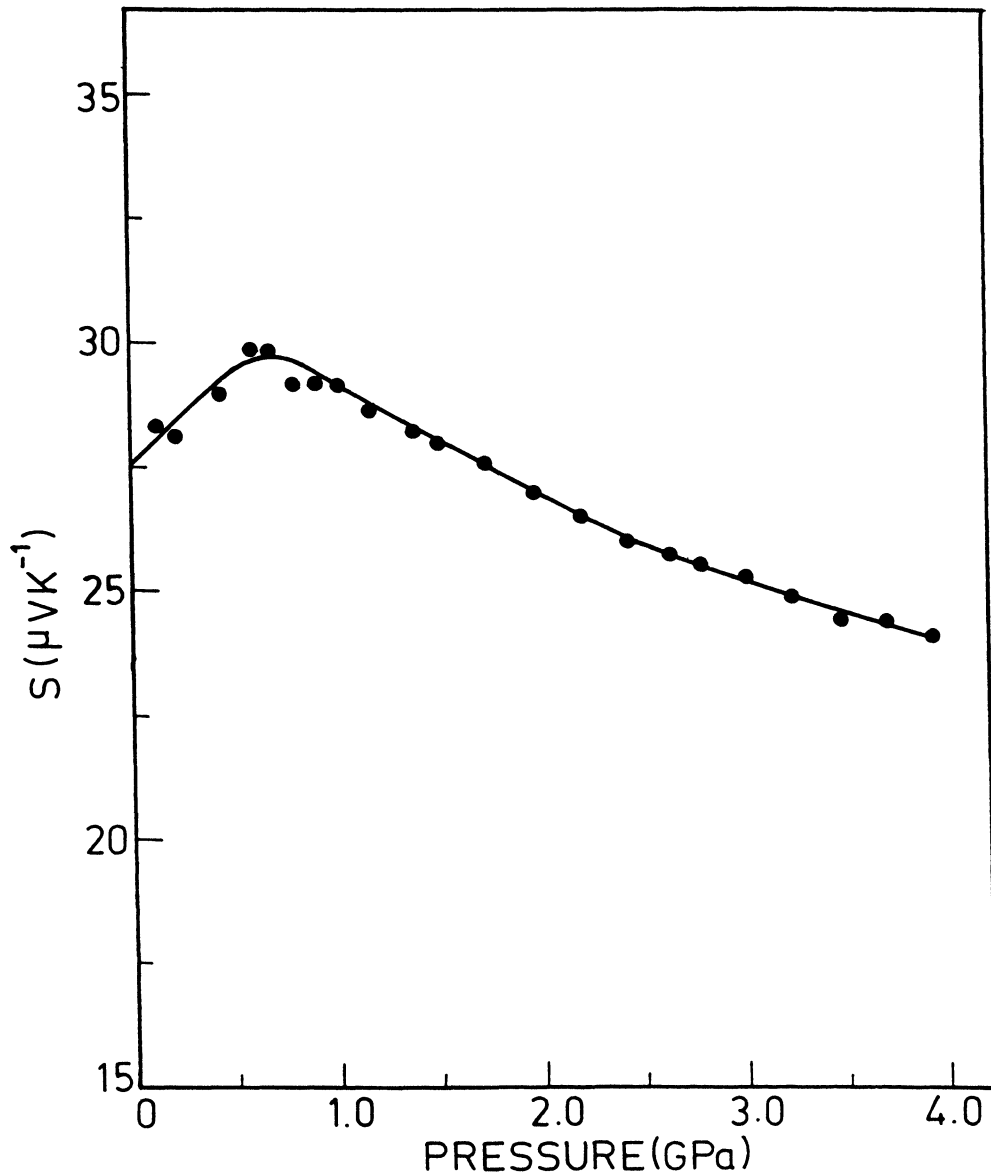


FIGURE 3 TEP vs Pressure of cold-pressed sample with  $x = 0.21$  in the direction of applied load.

#### 124 Samples

All the lines in the x-ray diffraction pattern could be indexed based on the a-centered orthorhombic cell with parameters  $a = 3.8337$ ,  $b = 3.8523$  and  $c = 27.1734 \text{ \AA}$ . The  $T_c$  was around 71 K.

The pressure dependence of TEP at room temperature is shown in fig. 4. TEP decreases with increasing pressure, starting with a value of  $16 \mu\text{VK}^{-1}$  at 1 atm.,

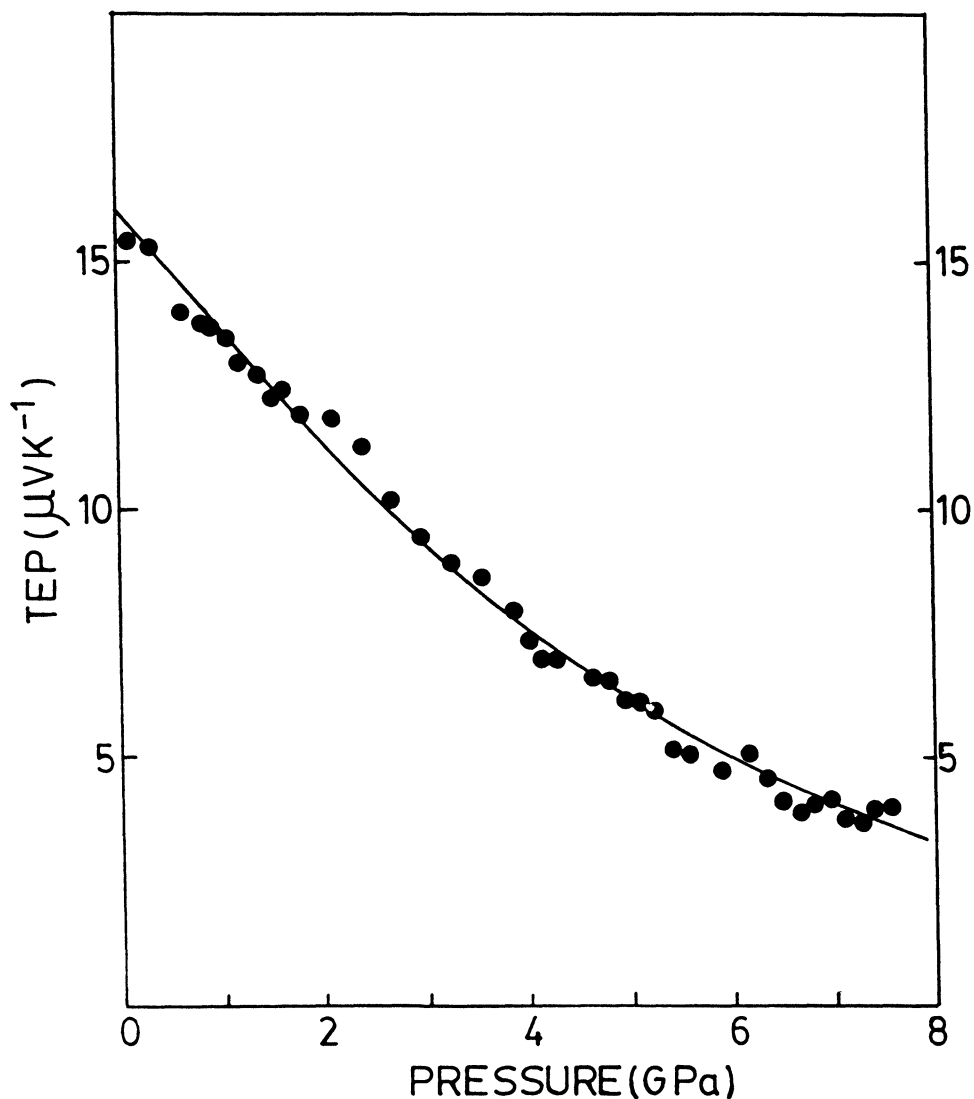


FIGURE 4 TEP vs Pressure data of 124 sample.

and reaches a value of  $3.5 \mu\text{VK}^{-1}$  at 8 GPa. TEP decreases at a rate of  $2.2 \mu\text{VK}^{-1} \text{GPa}^{-1}$  up to 4.5 GPa and at a slower rate of  $0.94 \mu\text{VK}^{-1} \text{GPa}^{-1}$  with further increase in pressure. Resistivity<sup>20</sup> and susceptibility<sup>21</sup> measurements as a function of pressure indicate that  $T_c$  increases sharply up to 5 GPa: beyond this pressure  $T_c$  varies slightly. X-ray diffraction data<sup>22</sup> is available up to 5 GPa and neutron diffraction<sup>23</sup> data up to 1 GPa. It is found that the z-coordinates of Ba, Cu(2), O(1) and O(4) change appreciably under pressure. However, because the TEP measurements were made on polycrystalline samples it is difficult to estimate the effect of the ionic movement under pressure on the TEP along the c-axis.

## CONCLUSION

We have made TEP measurements as a function of pressure on polycrystalline 123 and 124 and single-crystal 123 samples. In the single crystals, the TEP in the ab-plane decreased steadily with increase in pressure, whereas along the c-axis TEP showed a broad maximum around 1.5 GPa and decreased with further increase in pressure. Crystallite orientation effects were clearly observed in the polycrystalline 123 samples. The TEP of the polycrystalline 124 sample decreased sharply up to 4.5 GPa, beyond which the change in TEP was small, similar to the behavior of  $T_c$  under pressure in this system.

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## REFERENCES

1. M.F. Crommie, A. Zettl, T.W. Barbee III and M.L. Cohen, *Phys. Rev.* *B37*, 9734 (1988).
2. Z.Z. Wang and N.P. Ong, *Phys. Rev.* *B38*, 7160 (1988).
3. I.G. Gorlova, S.G. Zybtev and Y.I. Latyshev, *JETP Lett.* *47*, 672 (1988).
4. L. Forro, M. Raki, J.Y. Henry and C. Ayache, *Solid State Commun.* *69*, 1097 (1989).
5. M. Sera, S. Shamoto and M. Sato, *Solid State Commun.* *68*, 649 (1988).
6. S.W. Tozer, A.W. Kleinsasser, T. Penney, D. Keiser and F. Holtzberg, *Phys. Rev. Lett.* *59*, 1768 (1987).
7. S.J. Hagen, Z.Z. Wang and N.P. Ong, *Phys. Rev.* *B40*, 9389 (1989).
8. A. Driessen, R. Griessen, N. Koeman, E. Salomons, R. Bronwer, D.G. DeGroot, K. Heeck, H. Hemmes and J. Rector, *Phys. Rev.* *B36*, 5602 (1987).
9. J. Keneko, H. Yoshida, S. Abe, H. Morita, K. Noto and H. Fujimori, *Jpn. J. Appl. Phys.* *26*, L1374 (1987).
10. Y. Akahama, S. Endo, S. Noguchi and K. Okuda, *Jpn. J. Appl. Phys.* *26*, L871 (1987).
11. B. Okai, K. Takahashi and M. Ohta, *Jpn. J. Appl. Phys.* *26*, L820 (1987).
12. W.H. Feitz, M.R. Dietrich and J. Ecke, *Z. Phys.* *B69*, 17 (1987).
13. J.S. Olsen, S. Steenstrup, I. Johannsen and L. Gerward, *Z. Phys.* *B72*, 165 (1988).
14. P. Murugaraj, J. Maier and A. Rabenau, *Solid State Commun.* *71*, 167 (1989).
15. S.K. Ramasesha and A.K. Singh, *Bull. Mater. Sci.* *14*, 767 (1991).
16. S.K. Ramasesha and A.K. Singh, *Rev. Sci. Instrum.* *62*, 1372 (1991).
17. A. Lusnikov, L.L. Miller, R.W. McCallum, S. Mitra, W.C. Lee and D.C. Johnson, *J. Appl. Phys.* *65*, 3136 (1989).
18. J.D. Jorgensen, S. Pei, P. Lightfoot, D.G. Hinks, B.W. Veal, B. Dabrowski, A.P. Paulikas, R. Kleb and I.B. Brown, *Physica C* *171*, 93 (1990).
19. M.F. Crommie, A.Y. Liu, A. Zettl, M.L. Cohen, P. Parilla, M.F. Hundley, W.N. Creager, S. Hoen and M.S. Sherwin, *Phys. Rev.* *B39*, 4231 (1989).
20. E.N. VanEenige, R. Griessen, R.J. Wijngaarden, J. Karpinski, E. Kaldis, S. Rusiecki and E. Jilek, *Physica C* *168*, 482 (1990).
21. D. Braithwaite, G. Chouteau, G. Martinez, J.L. Hodeau, M. Marezio, J. Karpinski, E. Kaldis, S. Rusiecki and E. Jilek, *Physica C* *178*, 75 (1991).
22. R.J. Nelmes, J.S. Loveday, E. Kaldis and J. Karpinski, *Physica C* *172*, 311 (1990).
23. Y. Yamada, J.D. Jorgensen, S. Pei, P. Lightfoot, Y. Kodama, T. Matsumoto and F. Izumi, *Physica C* *173*, 185 (1991).