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Raman spectra of Bi–Sr–Ca–Cu–O high temperature superconductors

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Two high-temperature superconducting BiSrCaCuO compounds were fabricated as $Bi_{2.1}Sr_4Ca_4Cu_3O_{10+\delta}$ and $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$. The X-ray diffraction patterns of both the compounds show that $Bi_{2.1}Sr_4Ca_4Cu_3O_{10+\delta}$ contains predominantly the high T_c 2223 phase, and $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ the low T_c 2212 and high T_c 2223 phases, in equal amounts. The Raman spectra of these samples exhibit broad bands in the 430–512 cm^{-1} region, as in the lead-substituted 2212 phase. Change in configuration due to the presence of the 2223 phase in the sample is indicated by the broadening of the 465 cm^{-1} line. New bands at 611 and 678 cm^{-1} are observed. Peaks in the 430–512 cm^{-1} region exhibit a softening when the temperature is reduced to 93 K.

1. Introduction

The bismuth-cuprate system (BSCCO) is the first multiphasic superconducting system exhibiting a zero-resistance transition temperature, T_c, above 100 K [1]. A high T_c phase with a composition of $Bi_2Sr_2Ca_2Cu_3O_y$ (2223) and T_c of 110 K coexists with a low T_c phase, 85 K, of composition $Bi_2Sr_2Ca_1Cu_2O_y$ (2212). It was found that excess Cu^{2+} and/or both calcium and copper facilitate the evolution of the 2223 phase [2–5].

The general formula of the BiSrCaCu oxide system is $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$. There are one, two, three or four square planar Cu–O layers sandwiched between bismuth oxide layers in these compounds. The superconducting transition temperature, T_c, is generally found to increase with increasing n, where n is the number of such Cu–O layers [6, 7]. When $n = 1$, Bi 2201 with a T_c of 90 K and for $n = 3$, Bi 2223 with T_c of 110 K, are obtained. To achieve the stabilization of $n = 3$ members, a partial substitution of Bi/Ca by lead is found to be necessary [8].

The role of phonons and low-energy excitations in the mechanism of high T_c superconductivity is currently of much interest. Hence, considerable effort has been devoted to the study of infrared and Raman spectra of these materials [9]. Raman and IR studies help in probing the structure of the materials and contribute to the study of lattice vibrations. Such investigations can help to discriminate impurity phases (if they exist), from the superconducting phases. They may be important in understanding the superconducting mechanism [10].

Bismuth–copper oxide superconductors have been studied by several investigators [11–25]. This includes a number of studies on single crystals of 2212 phase ($Bi_2Sr_2CaCu_2O_{8+n}$). A superconducting gap value of $2\Delta = 209$ cm^{-1} (from BCS theory) has been determined by Sugai *et al.* [14] and a value of $2\Delta \sim 330$ cm^{-1} by Boekholt and Guntherodt [25]. Recently, Martinez *et al.* [24] have investigated the *a–b* anisotropy in $Bi_2Sr_2CaCu_2O_8$ using Raman active phonons. Raman spectra of ceramic BiSrCaCuO superconductors containing different phases other than 2212 have also been reported. Of these, Sapriel *et al.* [18] have reported the Raman spectra of BiSrCaCuO ceramic samples containing 15%–20% of the 2223 phase. They have not observed any additional lines with respect to the spectrum of a single crystal of 2212 phase. The incident light impinging on the ceramics will have a probability of falling on the *c*-phase of a thin plate on the ceramic surface. Therefore, according to Sapriel *et al.* [18] the spectrum is similar to that of the *c*-oriented single crystal of the 2212 phase. Cardona *et al.* [11] investigated the Raman spectra of $Bi_2(Sr_{1-x}Ca_x)_{n+2}Cu_{n+1}O_{(6+2n)+\delta}$ (where $n = 0, 1$), and have assigned some of the bands. The band at 465 cm^{-1} was assigned to the oxygen atom that bridges the BiO and CuO_2 planes. Boekholt and Guntherodt [26] have attributed this mode to the in-phase, out-of plane vibrations of the same oxygen atoms relative to the copper atoms (CuO_2 planes) while Iliev and Hadjiev [27] attribute it to the out-of-phase vibrations of the same oxygen atoms. The single-crystal spectra of the 2212 compound recorded by Farrow *et al.* [28] show major differences from those of Cardona *et al.* [11]. When lead is substituted for bismuth to obtain the high T_c 2223 phase, no continuous variation of this mode (465 cm^{-1}) with lead concentration is observed, necessitating further investigations [29]. The 630 cm^{-1} band has been assigned to the oxygen vibrations of the BiO planes. In this work, the T_c values, X-ray diffraction patterns and the Raman spectra of two high-temperature superconductors, $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ and $Bi_{2.1}Sr_4Ca_4Cu_3O_{10+\delta}$ were investigated.

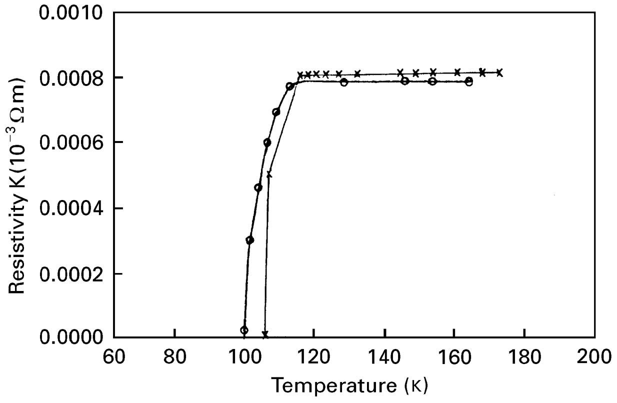

Figure 1 Plot of electrical resistivity versus temperature for BSSCO compounds. (*) Sample I, (O) Sample II.

2. Experimental procedure

The compounds $Bi_{2.1}Sr_4Ca_4Cu_3O_{10+\delta}$ and $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ were prepared by the conventional solid-state reaction technique [30]. High-purity powders were used for the purpose. The matrix method was followed for synthesis. A homogeneous charge was first prepared by mixing appropriate amounts of $SrCO_3$, $CaCO_3$ and CuO. The charge was calcined at 930 °C in air for 16 h after which it was cooled, pulverized, pelletized and heated until the reaction was complete and a good homogeneity ensured. Appropriate amounts of the matrix and Bi_2O_3 were mixed, pelletized and reacted at 1113 K for 3–5 min until the mass turned completely black. The process of grinding was repeated a couple of times. The samples were pelletized by applying a pressure of 10 ton cm^{-2} and finally sintered for 4 h at 1098 K. Later the samples were furnace cooled to room temperature.

Electrical resistance was measured as a function of temperature using the standard four-probe technique [31] (Fig. 1). Electrical contacts were made using an air-drying silver paste. Temperature was monitored using a copper constantan thermocouple. The voltage corresponding to ΔT was monitored with a resolution of 0.01 μV by a Keithley model 181 nanovoltmeter. A low-temperature cell and a 10 mA current source were also employed to measure the d.c. electrical resistance. X-ray diffraction analysis was performed using CuK_α radiation on a Japan Rigaku diffractometer. Raman spectra were recorded on a 1401 SPEX Raman spectrometer using a Spectra Physics model 165 Ar^+ laser at the room temperature (296 K) and at 93 K, with a resolution better than 5 cm^{-1}. A low-temperature cell was used to record the Raman spectra at 93 K. A RTD Pt 100 fitted inside the cold finger of the cell measured the temperature of the sample pellets attached to the cold finger. Both 515.5 and 488.0 nm lines of the laser were used. At room temperature, Raman spectra were also recorded with the samples taken in a capillary tube.

3. Results and discussion

Both the compounds, $Bi_{2.1}Sr_4Ca_4Cu_3O_{10+\delta}$ and $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$, exhibit high transition temperatures. For $Bi_{2.1}Sr_4Ca_4Cu_3O_{10+\delta}$ there is a sharp fall in resistivity at 105 K, and $R(0)$ has been recorded at the same temperature. In $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$, the T_c onset is at 105 K and the resistivity drops to zero at 100 K.

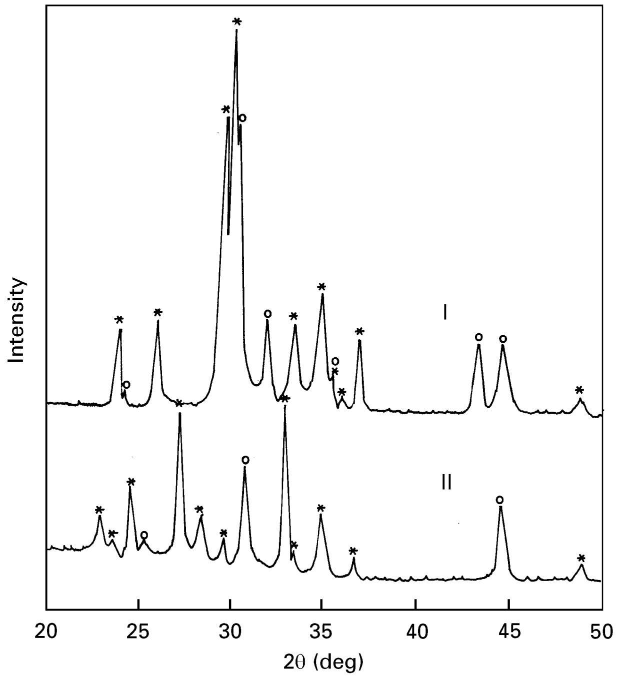

Figure 2 XRD patterns of samples I and II. (*) High T_c, (O) low T_c.

The XRD patterns of both the compounds show that they are of mixed phases where 2212 (low T_c) and 2223 (high T_c) phases are present. In $Bi_{2.1}Sr_4Ca_4Cu_3O_{10+\delta}$ (sample I), the 2223 phases are more prominent and in $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (sample II), the 2212 and 2223 phases are almost of the same intensity (Fig. 2).

The samples were prepared a number of times at the same processing temperature and yielded consistent results. The value of T_c and, in general, ρ versus T characteristics did not change even when current, I, was increased from 10 mA to 50 mA.

In the Raman spectra recorded at room temperature, $Bi_{2.1}Sr_4Ca_4Cu_3O_{10+\delta}$ exhibits peaks at 122, 190, 210–215 (broad band) 330, 440, 470 (broad band from 435–510 cm^{-1}) 550, 611 and 678 cm^{-1}. $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ has peaks at 122, 200, 228, 239, 290, 350, 378, 430–512 (broad band with peaks at 430, 440, 450, 465, 505, 512), 557 and 640 cm^{-1} with very weak bands at 611 and 680 cm^{-1} (Table I).

The 465 and 630 cm^{-1} lines are the most prominent in the Raman spectra of the BSCCO system [28]. In sample I ($Bi_{2.1}Sr_4Ca_4Cu_3O_{10+\delta}$, Fig. 3) there is a broad band in the 435–510 cm^{-1} region with peaks at 440 (broad), 470 and 490 cm^{-1}. The 640 cm^{-1} band is not observed, but bands are obtained at 611 and 678 cm^{-1}. In sample II (Fig. 4), there is a broad band in the 430–510 cm^{-1} region with peaks at 440, 450, 465, 505 and a band at 640 cm^{-1}. Only very weak bands are seen at 611 and 680 cm^{-1}. The 465 cm^{-1} band is assigned to a collective motion parallel to the c-axis of oxygen atoms surrounding bismuth atoms [11, 32, 33]. It has A_{1g} symmetry and it shows a softening of the phonon frequency with an onset just

TABLE I Raman bands of $Bi_{2.1}Sr_4Ca_4Cu_3O_{10+\delta}$ and $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ at 296 K

Temperature (K)	Sample I $Bi_{2.1}Sr_4Ca_4Cu_3O_{10+\delta}$	Sample II $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$
296	122	122
	190	200
	210–215	228
	(broad band)	
	330	239
	440	290
	470	350
	490	378
	435–510	430–512
	(broad band)	(broad band)
	550	450
	611	465
	678	505
		512
		557
		611
		640
		(weak)
		680

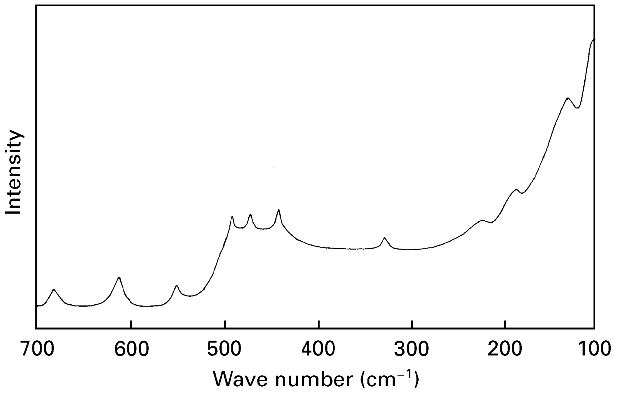

Figure 3 Raman spectrum of sample I at 296 K.

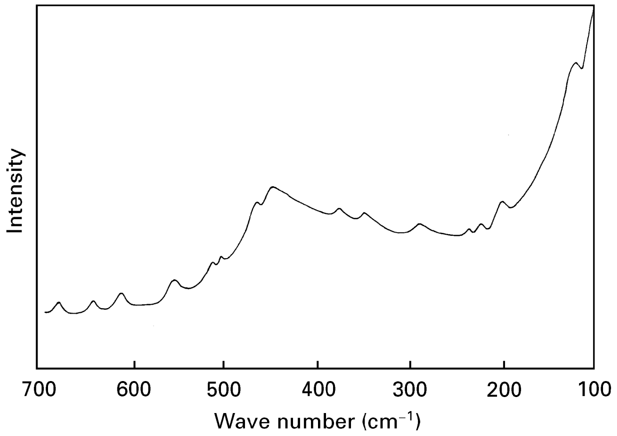

Figure 4 Raman spectrum of sample II at 296 K.

TABLE II Raman bands of $Bi_{2.1}Sr_4Ca_4Cu_3O_{10+\delta}$ and $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ at 93 K

Temperature (K)	Sample I $Bi_{2.1}Sr_4Ca_4Cu_3O_{10+\delta}$	Sample II $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$
93	122	121
	190	193
	203	203
	207–214	207–225
	285	245
	335	255
	459	325
	(weak)	
	480	425
	(weak)	
	612	435–455
		465
		490
		650

below T_c. This band is also considered as the vibrations of the oxygen atoms that bridge the BiO and CuO_2 planes [11, 32]. In lead-substituted 2212 phase single crystals, the 465 cm^{-1} line is observed as a wide band from 450–570 cm^{-1} with peaks at 460 and 530 cm^{-1}. Sapriel *et al.* [19] have interpreted this as due to the strengthening of the binding force between different planes due to the presence of lead atoms. Liarokapis *et al.* [29] have observed the sudden disappearance of the 465 cm^{-1} line when 30% Bi is substituted by lead. Another line appeared at 545 cm^{-1}. They did not observe a continuous variation in the intensity of this mode. Therefore, they do not support that the 465 cm^{-1} mode is associated with the vibration of the oxygen atoms that bridge copper and bismuth atoms. According to them, lead substitutes on other atomic sites (calcium or strontium atoms) in addition to bismuth, leading to a different configuration of oxygen atoms. Therefore, they associate the 465 cm^{-1} line with the out-of-plane vibrations of oxygen atoms in CuO_2 planes. As mentioned earlier, Boekholt and Guntherodt [25] also assign the mode to the out-of-plane vibration of oxygen atoms in the CuO_2 plane but in-phase. In both the samples used in the present study, broad bands are observed as in the lead-substituted 2212 phase. The high T_c 2223 phase is prominent in sample I and both the 2223 (high T_c) and 2212 (low T_c) phases are present in almost equal amounts in sample II. Change in configuration due to the presence of 2223 phase in the samples can be attributed to the broadening of the 465 cm^{-1} line. The number of CuO_2 layers is greater in the 2223 phase than in the 2212 phase. Sapriel *et al.* [19] have pointed out that additional copper–oxygen layers will lead only to Raman inactive lines. However, additional copper–oxygen layers and calcium layers can exert long-range forces, leading to the broadness of the line observed.

When the temperature is reduced to 93 K below T_c, the intensity of the Raman peaks is considerably reduced. Even the laser plasma lines obtained in the spectra appear with lesser intensity. Some of the bands disappear and the broad band in the 435–510 cm^{-1} region completely disappears in the spectrum of sample I. Only two weak bands at 459 and 480 cm^{-1} are observed. In sample II, weak bands are obtained at 425, 435–455 (broad) and 465 cm^{-1}. A faint broad band is also observed in sample II. Bands show a softening when compared to bands observed at 296 K. Boekholt *et al.* [21] have observed softening of the 463 cm^{-1} mode below the transition temperature.

Lines in the 630–660 cm^{-1} region are oxygen-related vibrations in BiO planes. In sample II, this peak is observed at 640 cm^{-1}, while in sample I there are two lines, one at 611 cm^{-1} and another at 678 cm^{-1}. The intensity of this line is found to be less than that observed by Sapriel *et al.* [18] in ceramic samples. The variation in the intensity of this line has also been noted both by Cardona *et al.* [11] and by Sapriel *et al.* [18]. But in sample I, which has a prominent 2223 phase, this line is observed at 611 and 678 cm^{-1}. Sapriel *et al.* [34] have noted the disappearance of the 650 cm^{-1} line and the increase in intensity of the 630 cm^{-1} line in lead-doped 2212 crystals. The disappearance of the 650 cm^{-1} line which is identified with the 2201 phase is interpreted by them as due to the removal of the 2201 phase with increased lead doping. Sapriel *et al.* [18] have shown the peak at 611 cm^{-1} to be due to the minority phase $Bi_2Ca_1Sr_2O_x$. But the same spectrum does not show the broad band in the 435–510 cm^{-1} region as in sample I. Other minority phases $Ca_{0.6}Sr_{0.4}Cu_{1.75}O_3$ and $(Ca_{0.9}Sr_{0.1})_2CuO_3$ also have no broad band in this region. Therefore, the 611 cm^{-1} band observed in sample I can be taken as due to the 2223 phase in comparison with the X-ray diffraction data.

In the Raman spectrum at 93 K, the 678 cm^{-1} band disappears and a weak band is obtained at 612 cm^{-1} in sample I, while in sample II, the very weak bands at 612 and 680 cm^{-1} disappear and the 640 cm^{-1} band is visible near the 650 cm^{-1} region. In this region too, the intensity of the bands is considerably reduced.

The strongest mode in the spectrum of the BiSrCaCuO system is at 122 cm^{-1} (Fig. 5). This mode originates from the vibration of copper atoms normal to the Cu–O plane. According to Sapriel *et al.* [34] the 122 cm^{-1} mode is due to a collective motion of copper and strontium atoms. Boekholt and Guntherodt [25] assign this mode to the vibrations of the strontium atoms. The 122 cm^{-1} line is prominent in both the samples of the present study, but with a lesser intensity than the intensity observed earlier [12, 18]. In the Raman spectra at 93 K, this mode appears in the same region with intensity considerably reduced. Popovic *et al.* [12] have found this mode at 130 cm^{-1} in $Bi_2(Sr_{1-x}Ca_x)_2CuO_{6+\delta}$.

The line at 290 cm^{-1} in sample II corresponds to the 2212 phase and this is absent in sample I, confirming the less prominent 2212 phase. This is a band of low intensity even in 2212 crystals. The phonons at 290 and 313 cm^{-1} are assigned to the bond bending vibrations of the O_4 and O_5 atoms in the BiO layers because of the incomplete occupation of the O_5 sites in the 2212 phase [24]. A band is observed at 330 cm^{-1} in sample I of high T_c 2223 phase. While this is absent in sample II, a band appears at 290 cm^{-1} in the Raman spectrum at room temperature.

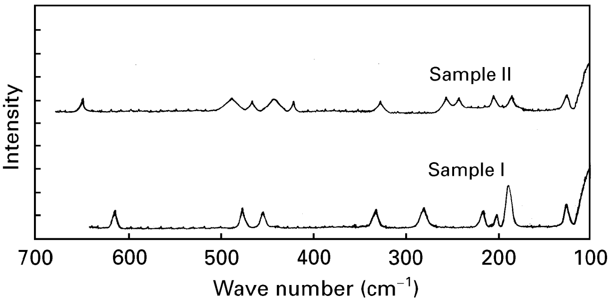

Figure 5 Raman spectra of BSCCO compounds at 93 K.

Cardona *et al.* [11] have assigned the band at 219 cm^{-1} to the "forbidden" A_g mode associated with strontium or copper atoms vibrating along *y*. This is observed as a broad band in the 210–215 cm^{-1} region in sample I and as a broad band with peaks at 200, 228 and 239 cm^{-1} in sample II. Bands in this region have been observed earlier in the 2212 crystals and ceramics [19]. At 93 K also these bands are obtained in both the samples but with lesser intensity. An additional line at 190 cm^{-1} is observed in sample I corresponding to the A_g mode at 184 cm^{-1} observed by Cardona *et al.* [11]. Boekholt and Guntherodt [24] have assigned the 190 cm^{-1} mode to the motion of copper atoms.

The modes at ~ 390, 500 and 580 cm^{-1} are said to originate from the CuO and BiO vibrations [12]. A broad structure at 391 cm^{-1} is related to the in-phase vertical vibrations of the $O_{1,2}$ oxygens. In sample I, a broad band at 550 cm^{-1} is observed, while sample II has bands at 378 and 505 cm^{-1}.

Of the two high-T_c superconducting compounds, $Bi_{2.1}Sr_4Ca_4Cu_3O_{10+\delta}$ contains the high T_c phase predominantly, and $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ contains the 2223 and 2212 phase in equal amounts, as evinced by the XRD patterns and Raman spectra. The Raman spectra of these samples have broad bands in the 430–512 cm^{-1} region as in the lead-substituted 2212 phase. The broadening of the 465 cm^{-1} line is due to the presence of the 2223 phase.

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References

1. H. MAEDA, Y. TANAKA, M. FUKUTOMI and T. ASANO, *Jpn J. Appl. Phys.* **27** (1988) L209.
2. G. CALESTANI, C. RIZZOLI, G. D. ANDREETTI, E. BULUGGIU, D. C. GIORI, A. VALENTI, A. VERA and G. AMORETTI, *Phys. C* **158** (1989) 217.
3. N. KIJIMA, H. ENDO, J. TSUCHIYA, A. SUMIYAMA, M. MIZUNO and Y. OGURI, *Jpn J. Appl. Phys.* **27** (1988) L1852.
4. S. KOYAMA, U. ENDO and T. KAWAI, *ibid.* **27** (1988) L1861.
5. J. TSUCHIYA, H. ENDO, N. KIJIMA, A. SUMIYAMA, M. MIZUNO and Y. OGURI, *ibid.* **28** (1989) L1918.
6. J. M. WHEATLEY, T. C. HSU and P. W. ANDERSON, *Nature* **333** (1988) 121.
7. CHELLAM RAMAKRISHNAN, R. K. RAJARAM and N. KRISHNAMURTHY, *Solid State Commun.* **72** (1989) 555.
8. S. LOSCH, H. BUDIN, O. EIBL, M. HARTMANN, T. RENTSCHLES, M. RYGULA, S. KEMMLER-SACK and R. P. HUEBENER, *Phys. C* **117** (1991) 271.
9. OSCAR E. PIRO, J. A. GIUDA, N. E. MASSA, P. J. AYMONIO, E. E. CASTELLANO, H. C. BASSO, J. N. H. GALLO and A. A. MARTIN, *Phys. Rev.* **B39** (1989) 7255.

10. JINGGING LIU, YIFENG YAN, TANG ZHOU, GUANGCAN CHE, DAWEI CHANG, WEI CHEN, YANYUN WANG and ZHONGXIAN ZHAO, *Mod. Phys. Lett.* **B2** (1988) 707.
11. M. CARDONA, C. THOMSEN, R. LIU, H. G. VON SCHNERING, M. HARTWEG, Y. F. YAN and Z. X. ZHAO, *Solid State Commun.* **66** (1988) 1225.
12 Z. V. POPOVIC, C. THOMSEN, M. CARDONA, R. LIU, G. STANISIC, R. KREMER and W. KONIG, *ibid.* **66** (1988) 965.
13. AKIO YAMANAKA, TOSHINORI KIMURA, FUJIO MINAMI, KUON INOUE and SHUNJI TAKEKAWA, *Jpn J. Appl. Phys.* **27** (1988) L1902.
14. SHUNJI SUGAI, HIDENORI TAKAGI, SHIN-ICHI UCHIDA and SHOJI TANAKA, *ibid.* **27** (1988) L1290.
15. P. KNOLL, B. STADLOBER, M. PRESSL and N. BRNICEVIC, *Phys. C* **162–164** (1989) 1097.
16. PHAM V. HUONG, EUNOK OH-KIM, KEU HONG KIM, DON KIM and JAE SHI CHOI, *J. Less-Common. Metals* **151** (1989) 133.
17. E. FAULQUES, M. MATUS, H. KUZMANY and P. KNOLL, *ibid.* **151** (1989) 139.
18. J. SAPRIEL, L. PIERRE, D. MORIN, J. C. TOLEDANA, J. SCHNECK, H. SAVARY, J. CHAVIGNON, J. PRIMOT, C. DAGUET, J. ETRILLARD and H. BOYER, *ibid.* **151** (1989) 31.
19. J. SAPRIEL, L. PIERRE, D. MORIN, J. C. TOLEDANO, J. SCHNECK, H. SAVARY, J. CHAVIGNON, J. PRIMOT, D. DAGUET and J. ETRILLARD, *Phys. Rev.* **B39** (1989) 339.
20. AKIO YAMANAKA, FUJIO MINAMI and KUON INOUE, *Phys. C* **162–164** (1989) 1099.
21. M. BOEKHOLT, A. ERLE, P. C. SPLITTGERBER-HONNEKES and G. GUNTHERODT, *Solid State Commun.* **74** (1990) 1107.
22. M. BOEKHOLT and G. GUNTHERODT, *Phys. C* **165–166** (1990) 1231.
23. A. CROSSLEY, P. R. GRAVES and S. MYHRA, *ibid.* **176** (1991) 106.
24. S. MARTINEZ, A. ZWICK, M. A. RENUCCI, H. NOEL and M. POTEL, *ibid.* **200** (1992) 307.
25. M. BOEKHOLT and G. GUNTHERODT, *ibid.* **181** (1991) 179.
26. *Idem*, *ibid.* **169** (1990) 436.
27. M. N. ILIEV and H. G. HADJIEV, *ibid.* **157** (1989) 495.
28. L. A. FARROW, L. H. GREENE, J. M. TARASCON, P. A. BONNER and G. W. HULL, *Phys. Rev.* **B38** (1988) 752.
29. E. LIAROKAPIS, TH. LEVENTOURI, O. PAPAGEORGIOU, H. LU and F. D. MEDINA, *Mod. Phys. Lett.* **B26** (1991) 1751.
30. P. V. P. S. S. SASTRY, I. K. GOPALAKRISHNAN, A. SEQUEIRA, H. RAJAGOPAL, K. GANGADHARAN, G. M. PATHAK and R. M. IYER, *Phys. C* **156** (1988) 230.
31. H. C. MONTGOMERY, *J. Appl. Phys.* **42** (1971) 2971.
32. M. STAVOLA, D. M. KROL, L. R. SCHNEEMEYER, S. A. SUNSHINE, R. M. FLEMING, J. V. WASZCZAK and S. G. KOSINSKI, *Phys. Rev.* **B38** (1988) 5110.
33. C. THOMSEN and M. CARDONA, in "Physical Properties of High Temperature Superconductors", edited by D. M. Ginsberg (World Scientific, Singapore, 1989).
34. J. SAPRIEL, J. SCHNECK, J. F. SCOTT, J. C. TOLEDANO, L. PIERRE, J. CHAVIGNON, C. DAGUET, J. P. CHAMINADE and H. BOYER, *Phys. Rev.* **B43** (1991) 6259.

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