

# Structural distortion in $(\text{La},\text{Sr})_2\text{CuO}_4$ cuprates: an insight using luminescence and EPR probes

V.V.S.S. Sai Sundar, A. Karthikeyani, R. Jagannathan \*

*Luminescence Group, Central Electrochemical Research Institute, Karaikudi 630006 (T.N.), India*

Received 23 February 1998; in final form 11 June 1998

## Abstract

We have demonstrated that  $\text{Eu}^{3+}$  luminescence can be successfully employed as a local probe to explore the microscopic symmetry of the cationic sites in the  $\text{Sr}^{2+}$ -substituted lanthanum cuprate superconductor(s). It has been found that  $\text{Sr}^{2+}$  substitution in  $\text{La}_{1-x}\text{Sr}_x\text{CuO}_4$  ( $x \sim 0.4$ ) does not alter the microscopic symmetry of the cationic site(s). Further, using electron paramagnetic resonance spectroscopy we have demonstrated that the hole centers arising out of  $\text{Sr}^{2+}$  substitution are localized around  $\text{Cu}^{2+}$  site(s). © 1999 Elsevier Science B.V. All rights reserved.

## 1. Introduction

In the recent years the La–M–Cu–O quaternary system ( $M = \text{Ca}, \text{Sr}, \text{K}, \text{and Na}$ ) leading to several cuprate combinations has attracted considerable interest as high  $T_c$  superconductor system (HTC) [1–4]. In particular  $\text{La}_2\text{CuO}_{4+\delta}$  is of special interest for HTC applications wherein the superconducting property is achieved either through excess oxygen stoichiometry ( $\delta > 0.05$ ) or through excess hole doping by aliovalent cationic substitution [5].  $\text{La}_2\text{CuO}_4$  crystallizes in an orthorhombic symmetry with the lattice parameters being  $a = 5.406 \text{ \AA}$ ;  $b = 5.370 \text{ \AA}$  and  $c = 13.150 \text{ \AA}$  and the corresponding space-group symmetry is  $F_{mmm}$  [6]. The  $\text{La}_2\text{CuO}_4$  system, when  $\text{Sr}^{2+}$  is substituted moderately ( $x \sim 0.15$ ) for  $\text{La}^{3+}$ , shows significant increase in the critical temperature ( $T_c$ ). It has been found that  $T_c$  vs.  $\text{Sr}^{2+}$  doping

$0.05 < x < 0.35$  adopts an inverted parabola [7] and the aliovalent substitution results in orthorhombic to tetragonal structural distortion [8]. Further, this substitution leads to considerable change in the oxygen stoichiometry in the lattice [9]. However, to the best of our knowledge there is little information in the literature concerning whether or not the microscopic symmetry around the cationic sites gets modified as a result of the aliovalent substitution. In order to explore the cationic sites of the  $\text{Sr}^{2+}$ -substituted La cuprate system, we have employed  $\text{Eu}^{3+}$  luminescence as a spectral probe. This is possible using  $\text{Eu}^{3+}$  luminescence with the lanthanide ion having simple energy level structure coupled with several structural dependent transitions [10] that can easily occupy  $\text{La}^{3+}$  sites. Furthermore to gain insight on the  $\text{Cu}^{2+}$  center(s), in the  $\text{Sr}^{2+}$ -substituted system we have demonstrated that electron paramagnetic resonance (EPR) spectroscopy can be successfully employed and the results point out that the holes

\* Corresponding author. E-mail: ecms@cscecri.ren.nic.in

arising out of  $\text{Sr}^{2+}$  substitution are localized in the  $\text{CuO}_2$  sheets in good agreement with the theoretical predictions [11].

## 2. Experimental

Both polycrystalline  $\text{La}_{2-x}\text{Eu}_x\text{CuO}_4$  (LCO) and  $\text{La}_{1.6-x}\text{Eu}_x\text{Sr}_{0.4}\text{CuO}_4$  (LSCO) ( $x = 2 \text{ mol}\%$ ) cuprates were prepared using conventional solid state reaction method by calcining at  $900^\circ\text{C}$  for 12 h and at  $1050^\circ\text{C}$  for 24 h. In order to improve the reactivity of the powders the mixture(s) were ground several times in between the firing stages. Heating cycles were repeated till the  $\text{CuO}$  peaks disappeared in the X-ray diffraction (XRD) pattern(s). The  $\text{Eu}^{3+}$  concentration with respect to  $\text{La}^{3+}$  was restricted to 2 mol% to avoid the formation of any  $\text{Eu}^{3+}$  clusters and any possible cross-relaxational effects affecting the emission from higher  $^5\text{D}_J$  (with  $J > 0$ ) energy levels of  $\text{Eu}^{3+}$ . The cuprates phases obtained were examined for their phase purity on a JEOL (JDX-8030) powder X-ray diffractometer employing  $\text{CuK}_\alpha$  radiation in the two theta range  $20\text{--}80^\circ$ . Lattice parameters were refined using a standard least squares fitting program. Photoluminescence (PL) spectra were recorded using a Hitachi 650-10S fluorescence spectrophotometer. Though the cuprate samples prepared were black in color, luminescence signals characteristic of  $\text{Eu}^{3+}$  centers were recordable under optimum conditions (moderately higher excitation slit-widths (5 nm) of the fluorescence spectrophotometer used). Electron paramagnetic resonance (EPR) measurements were made as described earlier [12]. DPPH was used as the reference for magnetic field corrections.

## 3. Results and discussion

Room temperature XRD patterns of the well-crystallized powder samples can be indexed under an orthorhombic system. Earlier studies by Huang et al. [13] show that in the cuprate system, the orthorhombic to tetragonal system takes place at a  $\text{Sr}^{2+}$  doping level of  $x = 0.28$  [13]. However, we could index the pattern on the basis of a tetragonal system only after removing the (008) line. The least squares fitted lattice parameter values along with orthorhombic distortion are listed in Table 1. The lattice parameters reported agree well with the values reported in the literature. On replacing  $\text{La}^{3+}$  with  $\text{Sr}^{2+}$  for the composition  $\text{La}_{1-x}\text{Sr}_x\text{CuO}_4$  ( $x = 0.4$ ) a marginal variation in the volume (about 2%) is observed. Some weak extra peaks corresponding to  $\text{La}_2\text{SrCu}_2\text{O}_6$  as a minor secondary phase are observed. However this can be ignored for all practical purposes for its weak intensity and further owing to the absence of any characteristic PL and EPR signals from this phase. In this Letter we discuss the results of freshly prepared samples and that of the aged sample after heat treatment at  $800^\circ\text{C}$  for 1 h (1 week old sample kept in air under our laboratory conditions). This is because the aged samples when studied (as such) did not show any characteristic PL and EPR signals in line with the reports of deterioration of superconductivity due to aging [14].

### 3.1. $\text{Eu}^{3+}$ luminescence as probe

$\text{Eu}^{3+}$  ion having  $4f^6$  configuration shows several intense electronic transitions in the visible region. These transitions have sharp features arising out of well-shielded deep lying localized levels of the

Table 1

Least squares refined cell parameters for LCO and LSCO systems indexed under space group  $F_{mmm}$

Composition	Lattice parameters			Orthorhombic distortion	Volume ( $\text{\AA}^3$ )
	$a$ ( $\text{\AA}$ )	$b$ ( $\text{\AA}$ )	$c$ ( $\text{\AA}$ )		
$\text{La}_2\text{CuO}_4$ (JCPDS std)	5.363	5.409	13.170	0.04	382.04
$\text{La}_2\text{CuO}_4$	5.382	5.403	13.167	0.02	382.79
$\text{La}_{1.96}\text{Eu}_{0.04}\text{CuO}_4$	5.369	5.392	13.159	0.03	380.62
$\text{La}_{1.56}\text{Eu}_{0.04}\text{Sr}_{0.4}\text{CuO}_4$	5.318	5.339	13.213	0.002	370.60

f-electron configuration. Fig. 1 gives the photoluminescence emission spectra of  $\text{Eu}^{3+}$ -doped in LCO and LSCO systems for 250 nm UV excitation. It is important to mention that the excitation spectrum monitoring  $\text{Eu}^{3+}$  emission has a narrow band with a maximum around 250 nm ( $\sim 5$  eV). This band can be assigned to  $\text{Eu}^{3+}-\text{O}^{2-}$  ( $4f^7 2p^{-1}$ ) charge transfer (CTB) transition. However, it is important to note that usually this type of charge transfer transitions are observed in both the LCO and LSCO systems at still higher energies around 10 eV as reported by Uchida et al. [15]. In our opinion the considerable decrease observed in the energy for the  $\text{Eu}^{3+}-\text{O}^{2-}$  charge transfer transition can be explained with the help of Jørgensen's refined electron spin pairing energy theory (RESPT) [16,17]. From this theory we have that, for the lanthanide ions having half-filled/filled shell or close to that, the energy required for the charge transfer transition will be minimum. This is quite possible for the  $\text{Eu}^{3+}$  ion having  $4f^6$  configuration wherein the ligand to metal electron transfer will result in a  $4f^7 2p^{-1}$  state with the lanthanide in the half-filled electron configuration.

Although the  $\text{Eu}^{3+}$  ion has wealth of energy levels in the  $^5D_J$  manifold, usually the lowest  $^5D_0$  level is the dominant emitting level. This is because the excitation in the higher energy levels of  $^5D_J$  ( $J > 1$ ) is normally relaxed to the lowest level, viz.  $^5D_0$ , through high frequency vibrations of the host-matrix in which the  $\text{Eu}^{3+}$  ion is doped. However, this cuprate system seems to be exceptional, in that the  $\text{Eu}^{3+}$  luminescence spectrum shows emission from higher levels, viz.  $^5L_6$  and  $^5D_J$  ( $J > 1$ ) (Fig. 1a). This implies the number of phonons required is too high ( $\gg 2$ ) to bridge the gap between the lowest ( $^5D_0$ ) and higher ( $^5D_J$ ;  $J > 1$ ) levels (f–f levels) owing to the low frequency vibrations of the host matrix. This can be explained as possibly due to the host matrix having metallic character. This will lead to a situation where the multi-phonon relaxation process is minimal as can be visualized through the relation given by van Dijk and Schurmanns [18].

$$K_{\text{NR}} = \beta_{\text{el}} \exp[-(\Delta E_0 - 2\hbar w_{\text{max}})] \dots \quad (1)$$

where  $K_{\text{NR}}$  is the non-radiative relaxation rate;  $\alpha$  and  $\beta_{\text{el}}$  are the experimental constants characteristic of the host matrix;  $\Delta E_0$  is the energy gap between

the two levels considered;  $\hbar$  is the Planck constant and  $w_{\text{max}}$  is the maximum frequency of the host matrix.

Of the various f–f transitions of  $\text{Eu}^{3+}$  observed in the emission spectrum, the  $^5D_0 \rightarrow ^7F_2$  transition observed in the red region around 610–620 nm is the most important as it is a *hyper-sensitive transition*. This transition, occurring through an electric dipole mechanism, is expected to be absent in centro-symmetric surroundings of the host-matrix as the direct product concerning the ground and excited (f–f intra-configurational) states vanishes under an inversion operation [19]. Further, this transition is very sensitive to the chemical surroundings of the site it occupies [20]. On the other hand, the transitions with  $\Delta I = +1$  such as  $^5D_0 \rightarrow ^7F_1$  and  $^5D_1 \rightarrow ^7F_0$  have magnetic dipole character and are structure independent. For this reason these are used as internal standards in the analysis of a luminescence spectrum. In order to fix the symmetry of the site(s) occupied by  $\text{Eu}^{3+}$ , information on the Stark splitting pattern in the  $\text{Eu}^{3+}$  levels is necessary. The splitting pattern should be consistent with the structural details known of the host matrix or in exceptional cases a minor deviation is possible.

From the structural data available on the  $\text{La}_2\text{CuO}_4$  system we have that the lanthanide site(s) ( $\text{Ln}^{3+}$ ) can have two types of coordination. In particular the larger  $\text{La}^{3+}$  ion exhibits an anti-prismatic geometry with a nine-coordination (Fig. 1; inset) [6]. In this case, the presence of the ninth oxygen lowers the symmetry of the lanthanide site. Thus an orthorhombic symmetry  $C_{2v}$ , or still lower symmetry is anticipated. The smaller lanthanides ( $\text{Gd}^{3+}$ ,  $\text{Nd}^{3+}$ ) can have an eight coordinated site with regular Archimedean antiprismatic coordination with oxygen described a by  $D_{4h}$  point group symmetry having inversion center.

In order to explain the results obtained, in the  $\text{Eu}^{3+}$  emission spectrum we do observe an intense electric dipole transition in the region 610–620 nm (Fig. 1) and hence obviously we can not expect  $\text{Eu}^{3+}$  to occupy a centro-symmetric site. For the LCO system, moderately intense  $^5D_J \rightarrow ^7F_{J'}$  and  $^5D_0 \rightarrow ^7F_{J'}$  emissions with  $J, J' = 1, 2$  and 3 are observed. In the case of the Sr-substituted LSCO system, also an identical emission pattern with a two-fold increase in the emission intensity is observed.

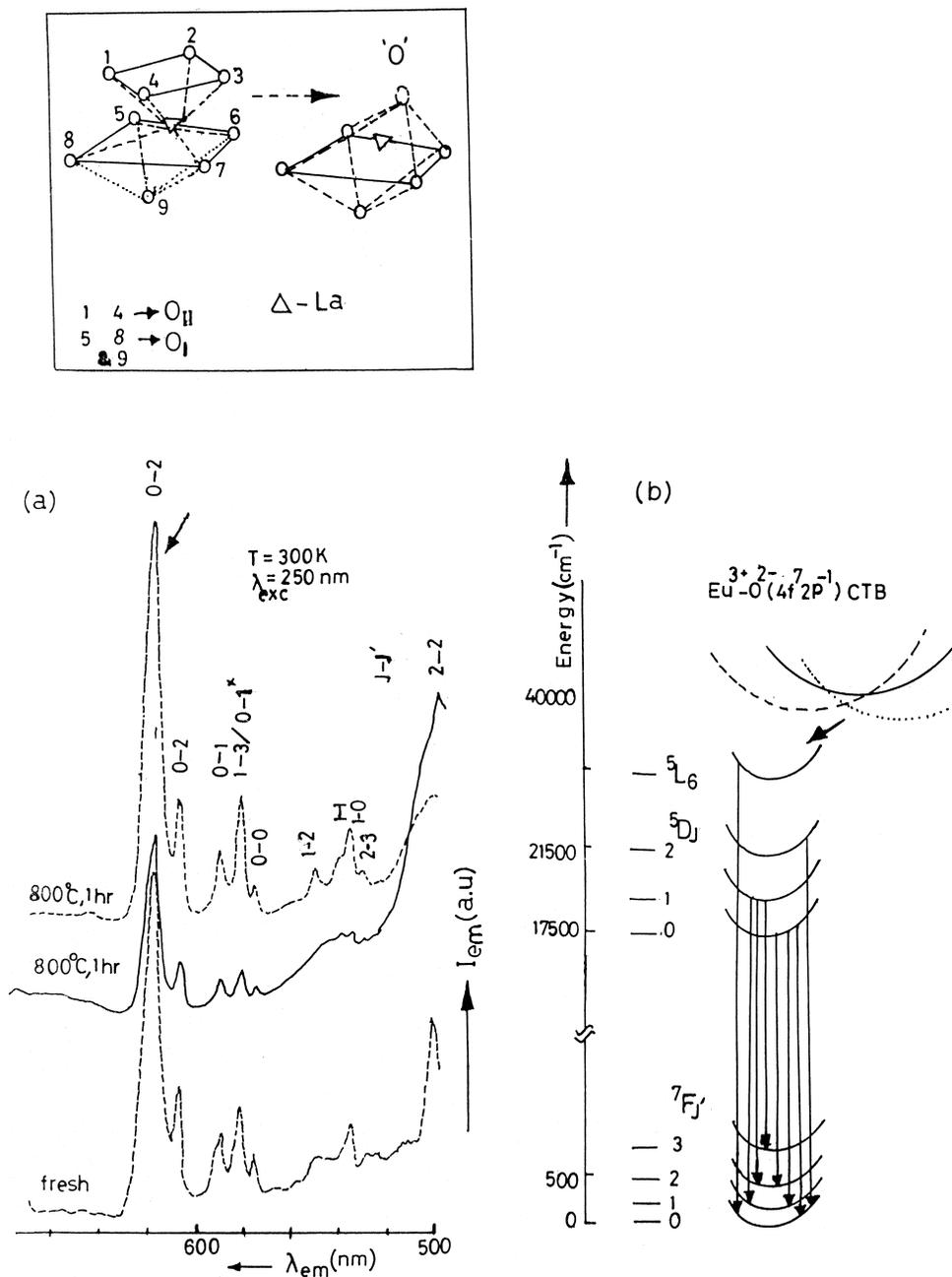


Fig. 1. (a) Photoluminescence spectra of  $\text{Eu}^{3+}$  (2 mol%) doped in La-cuprate (LCO – solid line) and LaSr-cuprate (LSCO – dashed line) corresponding to fresh and aged (1 week old after heat treatment at  $800^\circ\text{C}$  for 1 h) samples. The  $\times$  mark indicates the transition is less probable on intensity consideration. Inset: A nine coordinated (with oxygen ions)  $\text{La}^{3+}$  site turning out to be a site with 'O' symmetry. (b) Configurational coordinate diagram explaining the  $\text{Eu}^{3+}$  luminescence in this system. CTB refers to  $\text{Eu}^{3+}-\text{O}^{2-}$  charge transfer band with the solid CTB parabola corresponding to the undoped LCO: $\text{Eu}^{3+}$  system, while the dashed one indicates the LSCO: $\text{Eu}^{3+}$  system and the dotted parabola corresponds to the aged sample. Solid arrow indicates the feeding of excitation energy from CTB to various localized f-f levels of  $\text{Eu}^{3+}$ .

The Stark splitting pattern(s) of the prominent  ${}^5D_0 \rightarrow {}^7F_J$  transitions (in particular  $J' = 0, 1$  and 2) can explain the microscopic symmetry of the site it occupies as illustrated in Table 2. The non-degenerate  ${}^5D_0 \rightarrow {}^7F_0$  transition ( $J = 0$  to 0 forbidden) has only one weak component implying the absence of site multiplicity occupied by  $\text{Eu}^{3+}$  and the lack of a linear field term in the expression for the crystal field potential. It is significant to note that the presence of a strong linear field term will facilitate an intense  ${}^5D_0 \rightarrow {}^7F_0$  emission [21] and hence the weak transition observed excludes the possibility the site having  $C_{nv}$  or lower symmetry. The structure independent  ${}^5D_0 \rightarrow {}^7F_1$  magnetic dipole transition(s) has two components (considering the relative intensities, the more intense component should be assigned to  ${}^5D_1 \rightarrow {}^7F_3$  transition) while the  ${}^5D_0 \rightarrow {}^7F_2$  electric dipole transition has three components at 609, 616 and 620 nms. However, it should be noted that the Stark splitting between the latter two intense components is too fine to attribute to two components (marked by solid arrow in Fig. 1). Hence taking into consideration the Stark splitting pattern (Table 2) we predict a higher symmetry than can be expected from the structural information documented in literature [6,8]. A cubic group lacking a holohedrized symmetry element seems to be the most probable to fit the above splitting pattern, to be exact either  $T_d$  or O point-group symmetry. As the former is too low for the coordination considered this can be rejected and hence we fix the latter to be the most probable one to explain the above results. This may be possible for the  $\text{La}^{3+}$  ( $\text{Eu}^{3+}$ ) site in this system, especially when surrounded by nine oxygen ions as a covalent network. Here, it should be noted that from the structural data [6] we have the  $\text{La}^{3+}$  ion almost at the center of the layer of 4  $\text{O}_I$  atoms (marked 1–4 in Fig. 1; inset) capped by an apical oxygen (marked 9)

at one end, with the layer formed by the other four  $\text{O}_{II}$  oxygen ions (marked 1–4 in Fig. 1; inset) on the other side. It should be noted that the layer formed by the  $\text{O}_{II}$  oxygen ions is in a strong covalent bonding with  $\text{La}^{3+}$  center, as implied by the inter-ionic distances being much less than the sum of the ionic radii [22]. In our opinion, the strong covalent bonding due to 4 $\text{O}_{II}$  oxygen ions marked (1–4) works as though they form the other apex of the La-4 $\text{O}_I$  layer resulting in a polyhedron that can be described by ‘O’ point-group symmetry (inset of Fig. 1). This, we believe, works at least as the effective symmetry. In any case, it is quite obvious that the holes generated due to the  $\text{Sr}^{2+}$  substitution do not alter the microscopic symmetry of the  $\text{La}^{3+}$  site as can be concluded from the identical PL emission spectra in both the cases of LCO and LSCO.

More important, the conclusions drawn in this investigation using  $\text{Eu}^{3+}$  luminescence as a probe is considerably different from that which has been established through the results of crystallography [8,13]. The discrepancies being: higher symmetry predicted for the  $\text{La}^{3+}$  site and the structural invariance with  $\text{Sr}^{2+}$  doping (especially the microscopic symmetry of  $\text{La}^{3+}$  site being invariant). In order to explain these, the role of the anionic network around  $\text{La}^{3+}$  formed by the oxygen ions undergoing changes with the oxygen off-stoichiometry and the aliovalent substitution is crucial. In our opinion, for compounds having strong covalent bonds between the anions and the cation(s), when the changes in the anionic network are not limited to the first coordination sphere, the microscopic symmetry of the cationic site will remain intact. Further, through EPR results (discussed in Section 3.2) we have found that with  $\text{Sr}^{2+}$  substitution in the La-cuprate system, the holes are localized around  $\text{Cu}^{2+}$  center(s). This lends support to the conclusion that at least the first coordination

Table 2

Stark splitting pattern for various  $\text{Eu}^{3+}$  levels under various site symmetries in LCO and LSCO systems

Site symmetry	Splitting pattern for important transitions and number of Stark components in brackets			Remarks
	${}^5D_0 \rightarrow {}^7F_0$	${}^5D_0 \rightarrow {}^7F_1$	${}^5D_0 \rightarrow {}^7F_2$	
$O_h$	$A_{1g}^* (1)$	$T_{1g} (1)$	$A_{2g} + E_g^* (2)$	* – forbidden
$D_{4h}$	$A_{1g}^* (1)$	$A_{2g} + E_g (2)$	$A_{1g} + B_{1g} + B_{2g} + E_g^* (4)$	* – forbidden
$C_{2v}$	$A_1 (1)$	$A_2 + B_1 + B_2 (3)$	$2A_1 + A_2 + B_1 + B_2 (5)$	too low
O	$A_1 (1)$	$T_1 (1)$	$E + T_2 (2)$	probable

sphere of the  $\text{La}^{3+}$  is not disturbed even with  $\text{Sr}^{2+}$  substitution. To account for the higher symmetry for the  $\text{La}^{3+}$  site(s) predicted in this investigation we believe that the covalent bonding between the four  $\text{O}_{II}$  oxygen ions works as if the effective charge distribution of the layer is a single point charge, hence leading to a cubic symmetry for the lanthanide site.

Further it has been found that the  $\text{Eu}^{3+}$  emission intensity in the  $\text{Sr}^{2+}$ -doped (LSCO) system is two times higher than that in the LCO system (Fig. 1a). The enhancement in  $\text{Eu}^{3+}$  emission intensity with the  $\text{Sr}^{2+}$  substitution can be explained as follows: the substitution with the less electronegative alkaline-earth ( $\chi_{\text{Sr}^{2+}} = 0.9$ ;  $\chi_{\text{La}^{3+}} = 1.2$ ) will result in the lowering of Madelung energy of the system in turn leading to an inward shift of the CTB parabola. The inward shift in the CTB state (marked as dashed line in Fig. 1b) will increase the scope for effective feeding of the excitation energy to the lower lying  $^5\text{D}_j$  states resulting in the enhancement in  $\text{Eu}^{3+}$  emission intensity. The degradation in the  $\text{Eu}^{3+}$

emission intensity due to aging can be attributed to the creation of oxygen vacancies. This will result in the outward shift of the CTB parabola in the excitation spectrum (marked as dotted line in Fig. 1b) leading to luminescence quenching, thus accounting for the decreased luminescence intensity due to aging.

### 3.2. EPR as a local probe

As far as we are aware, there are no reports concerning the EPR of La-cuprates except the one by Saez Puche et al. [23]. This may be because of the metallic character of the system. In  $\text{La}_2\text{CuO}_4$ , Saez Puche et al. observed weak EPR signals at  $g$ -values of 2.06 and 3.04 and the weak signals were attributed to the metallic character of the cuprate system. Our results are also the same inasmuch as the absence of characteristic signals is concerned and hence we do not discuss the LCO system further.

On the other hand, for the case of the Sr-substituted LSCO system, we observed a drastic change

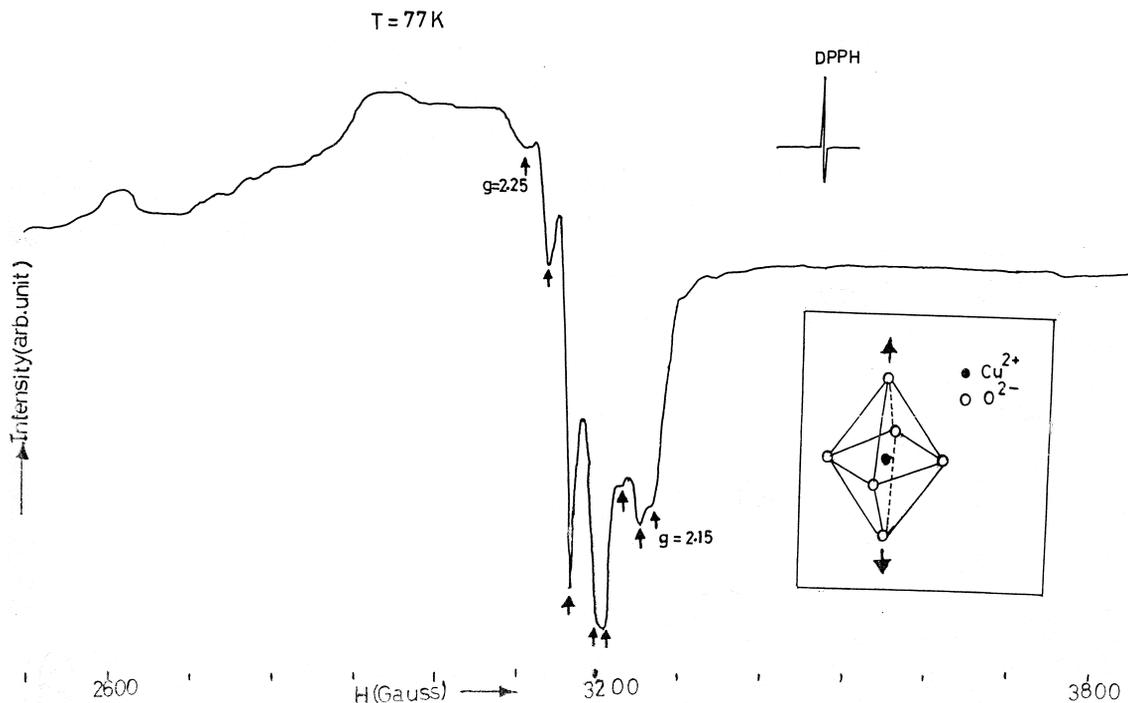


Fig. 2. X-band EPR spectra of fresh LSCO: $\text{Eu}^{3+}$  sample. DPPH is used for field correction. Inset:  $\text{Cu}^{2+}$  in a six-coordinated distorted octahedral site in LCO system. The arrows indicate elongation along the direction of apical oxygen ions.

in the EPR signals. For this system, we observe a characteristic 8-fold structure (marked by arrows in Fig. 2) with the  $g$ -values in the range 2.15 to 2.25, and the splitting between the two successive components is about 25–30 G.

From the structural details on the lanthanum cuprate unit cell, we have the  $\text{Cu}^{2+}$  center(s) in a distorted octahedral site (Fig. 2; inset) owing to the unusually larger elongation (about 29%) in the direction of the apices of the octahedral network of oxygen ions [6]. Further,  $\text{La}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Sr}^{2+}$  ions are non-paramagnetic and also their nuclear spins are too low to account for the 8-fold structure observed and hence the contributions from these ions can be discounted. On the other hand, the  $\text{Cu}^{2+}$  ion having  $d^9$  electron configuration works as though we have a hole in a filled d-shell. The higher  $g$ -values observed ( $g > 2.0036$ ) for the structure clearly reflect the involvement of holes and further the 8-fold structure observed could be the hyperfine structure contribution from the two isotopes of  $\text{Cu}^{2+}$  ( $^{63}\text{Cu}$  and  $^{65}\text{Cu}$ ) each having nuclear spin  $I = 3/2$ . This is consistent with the relation  $2(2I + 1) = 8$  hfs components observed. Moreover, the unusual hyperfine structure with decreasing linewidth and increasing amplitude for the components towards higher magnetic fields is characteristic of  $\text{Cu}^{2+}$  centers in a distorted octahedral site undergoing Jahn–Teller distortion and can be explained by the ‘rapid tumbling motion’ effect [24,25].

In all fairness, these observations enable us to propose that the hole centers are coupled with  $\text{Cu}^{2+}$  nuclei and hence are localised around  $\text{Cu}^{2+}$  centers. This is in good agreement with the theoretical model of Pokrovsky and Uimin predicting localization of holes in the  $\text{CuO}_2$  sheets of the Sr-doped La-cuprate system [11]. Finally, it is noteworthy that a recent paper by Hammel et al. [26] also confirmed the localization of holes in the  $\text{CuO}_6$  network, through NQR spectra in good agreement with our results.

#### 4. Conclusions

In conclusion we have demonstrated that  $\text{Eu}^{3+}$  luminescence and EPR probes can be successfully employed to gain insight on the various cationic sites of the LaSr cuprate system. The results being that the

$\text{La}^{3+}$  environments in both the cases of pure and  $\text{Sr}^{2+}$ -doped systems are identical and the hole-related defect centers are localized around  $\text{Cu}^{2+}$  center(s).

#### Acknowledgements

Our sincere thanks to Professor T.R.N. Kutty and Mr. Mohandass Nayak, I.I.Sc., Bangalore for the help in getting EPR data and also to the referee for the valuable comments on the earlier version of the manuscript.

#### References

- [1] J.B. Torrance, Y. Tokura, A.I. Nazzal, A. Bezinge, T.C. Huang, S.S.P. Parkin, *Phys. Rev. Lett.* 61 (1988) 1127.
- [2] M.A. Subramanian, J. Gopalakrishnan, C.C. Toradi, T.R. Askew, R.B. Flippen, A.W. Sleight, J.J. Liu, S.J. Poon, *Science* 240 (1988) 495.
- [3] K. Kishio, K. Kitazawa, S. Kaubne, I. Yasuda, N. Sagai, H. Takagi, S. Uchida, K. Fueki, S. Tanaka, *Chem. Lett.* 2 (1987) 429.
- [4] H. Shibata, K. Kinoshita, T. Yamada, *Physica C* 170 (1990) 411.
- [5] J.E. Schirber, B. Morosin, R.M. Merrill, P.F. Lava, E.L. Veuturini, J.F. Kwak, P.H. Barghman, D.S. Ginlay, *Physica C* 152 (1988) 121.
- [6] Hk. Muller-Buschbaum, *Angew. Chem.* 16 (1977) 681.
- [7] H. Takagi, T. Ido, S. Ishibashi, M. Uota, S. Uchida, Y. Tokura, *Phys. Rev. B* 40 (1989) 2254.
- [8] Y. Maeno, A. Odagawa, N. Kakehi, T. Suzuki, T. Fujita, *Physica C* 173 (1991) 322.
- [9] E.J. Opila, H.L. Tuller, *J. Am. Ceram. Soc.* 77 (1994) 2727.
- [10] G. Blasse, in: K.A. Gschneidner, L. Eyring (Eds.), *Handbook of Physics and Chemistry of Rare Earths*, Chap. 34, North-Holland, Amsterdam, 1979.
- [11] V.L. Pokrovsky, G.V. Uimin, *Physica C* 160 (1989) 320.
- [12] R. Jagannathan, T.R.N. Kutty, M. Kottaisamy, P. Jeyagopal, *Jpn. J. Appl. Phys.* 33 (1994) 6207.
- [13] T.C. Huang, J.B. Torrance, A.N. Nazzal, Y. Tokura, *Powd. Diffr.* 4 (1989) 152.
- [14] M.W. Shafer, T. Penney, B.L. Olson, *Phys. Rev. B* 36 (1987) 4047.
- [15] S. Uchida, T. Ido, H. Takagi, T. Arima, Y. Tokura, Y. Tajima, *Phys. Rev. B* 43 (1991) 7942.
- [16] L.J. Nugent, R.D. Baybarz, J.L. Burnett, J.L. Ryan, *J. Inorg. Nucl. Chem.* 33 (1971) 2503.
- [17] R.C. Ropp, *Luminescence and the Solid State Studies in Inorganic Chemistry*, Elsevier, 1991.
- [18] J.M.F. van Dijk, M.F.H. Schurmanns, *J. Chem. Phys.* 78 (1983) 5317.

- [19] D.H. Butler, *Point Group Symmetry Applications: Methods and Tables*, Plenum Press, New York, 1984.
- [20] S.F. Mason, B. Stewart, *Mol. Phys.* 55 (1985) 611.
- [21] W.C. Nieuwpoort, G. Blasse, A. Bril, in: H.M. Crosswhite, H.W. Moos (Eds.), *Optical Properties of Ions in Crystals*, Interscience Publishers, New York, 1967, p. 161.
- [22] C. Chaillout, J. Chenavas, S.W. Cheong, Z. Fisk, M. Marezio, B. Morosin, *Physica C* 170 (1990) 87.
- [23] R. Saez Puche, M. Norton, W.S. Glaunsinger, *Mater. Res. Bull.* 17 (1982) 1429.
- [24] A. Abragham, B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Clarendon Press, Oxford, 1970, p. 466.
- [25] R.E. Coffman, *J. Chem. Phys.* 48 (1968) 609.
- [26] P.C. Hammel, B.W. Stat, R.L. Martin, F.C. Chou, D.C. Johnston, S.W. Cheong, *Phys. Rev. B* 57 (1998) R712.