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## ITINERANT ELECTRON FERROMAGNETISM IN $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ : A MÖSSBAUER STUDY

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**Résumé.** — Des études par effet Mössbauer et par d'autres méthodes montrent que dans  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  ( $x > 0,125$ ), des agrégats ferromagnétiques riches en  $\text{Sr}^{2+}$  coexistent dans une même phase cristallographique avec des régions paramagnétiques riches en  $\text{La}^{3+}$ , la composante ferromagnétique augmentant quand  $x$  augmente et quand  $T$  diminue. Les trous 3d créés par substitution de  $\text{Sr}^{2+}$  sont itinérants, aussi bien au-dessus qu'en dessous de  $T_c$ , comme il ressort de la conductivité électrique et du coefficient de Seebeck. Toutes les observations expérimentales concernant ce système peuvent être expliquées sur la base de ferromagnétisme électronique itinérant.

**Abstract.** — Mössbauer and other studies establish that in  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  ( $x < 0.125$ ), ferromagnetic  $\text{Sr}^{2+}$  rich clusters coexist with paramagnetic  $\text{La}^{3+}$  rich regions in the same crystallographic phase, with ferromagnetic component increasing with increasing  $x$  and decreasing  $T$ . The 3d holes created by  $\text{Sr}^{2+}$  substitution are itinerant both above and below  $T_c$  as evidenced by electrical conductivity and Seebeck coefficient. All the experimental observations on this system can be explained on the basis of itinerant electron ferromagnetism.

**1. Introduction.** — A detailed study of rare earth cobaltates employing Mössbauer spectroscopy as well as magnetic, electrical and other measurements reported recently by us has provided a picture which explains structural changes in and magnetic and transport properties of these cobaltates and has indeed shown conclusively that the first order endothermic transition observed in these cobaltates in the range 1000-1200 K can be characterized as localized  $\rightleftharpoons$  collective electron transition [1-3]. This paper deals with a novel oxide system  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ;  $0 < x \leq 0.5$ , the end member of which is  $\text{LaCoO}_3$ .

Jonker and van Santen [4] first observed that  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  becomes ferromagnetic for  $x > 0.15$  and associated it with the concentration of tetravalent Co with increasing  $\text{Sr}^{2+}$  substitution. However, the magnitude of magnetic moment and the paramagnetic Curie temperature could not be satisfactorily explained. Goodenough [5] assuming the 3d electrons to be localized interpreted the ferromagnetic behaviour by modifying the superexchange model of Anderson [6]. However, he himself later on pointed out that covalent mixing between the transition metal d orbitals and oxygen 2p orbitals may enhance the superexchange interaction sufficiently to break down the conditions for localized d electrons [7]. It is now known that delocalization of d electrons is very much prevalent in transition metal oxides, particularly in those with perovskite structures than suspected earlier [1-3, 7]. Several conceptual problems remained unexplained such as for example the mechanism of ferromagnetism, the development of ferromagnetic clusters in the

paramagnetic matrix as Sr concentration is increased, simultaneous initiation of ferro-magnetism and itinerant electron behaviour, etc.

This paper deals with Mössbauer effect studies and other measurements on this system. These studies have clearly brought out that ferromagnetic  $\text{Sr}^{2+}$  rich clusters which grow in size with Sr concentration and decreasing temperature coexist with paramagnetic  $\text{La}^{3+}$  rich region in the same crystallographic phase. Further, these studies have shown that the 3d holes created on Sr substitution are itinerant both above and below  $T_c$  and that itinerant electron ferromagnetism is responsible for ferromagnetism in the system.

**2. Experimental.** — Samples of  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  with various values of  $x$  were prepared by coprecipitating the oxalates in the required proportion essentially following the method described earlier [1, 8]. All the samples were checked for stoichiometry by using thermogravimetry. X-ray diffraction, paramagnetic susceptibility, differential thermal analysis and electrical transport property measurements were carried out using standard equipment. For Mössbauer spectroscopy, these samples were used as sources prepared by thermal diffusion of  $\text{Co}^{57}$  in the pellets of  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  or by incorporating  $\text{Co}^{57}$  in the oxalates themselves before synthesizing the compounds. These sources were matched against 310 ESS or  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3 \text{H}_2\text{O}$  (KFCN) single crystal absorbers. The observed spectra were fitted to machine computed Lorentzians.

**3. Results and discussion.** — Mössbauer spectra of  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  for  $0 < x \leq 0.5$  matched against KFCN at room temperature and against 310 ESS at 78 K are shown in figures 1 and 2. Our most important observations on this system are the following :

3.1 In the interval,  $x \leq 0.125$ , the paramagnetic Mössbauer spectra resolve, at all temperatures, into two resonances which can be assigned to two different valence states of iron, namely, high spin trivalent iron  $\text{Fe}^{3+}$  and low spin tetravalent iron  $\text{Fe}^{\text{IV}}$  arising out of the corresponding spin states of cobalt.

3.2 At no values of  $x$  in the solid solution interval  $0.125 < x \leq 0.5$  did we observe a Mössbauer resonance that could be uniquely identified as belonging to the tri- and tetravalent iron. Indeed at all temperatures, the spectra could be identified to a valence state lying in between  $\text{Fe}^{3+}$  and  $\text{Fe}^{\text{IV}}$ .

3.3 Compositions in the interval  $0.125 < x \leq 0.5$  exhibit ferromagnetically split spectrum at low temperatures. The Mössbauer spectra give one set of six finger pattern at 78 K with hf field of  $320 \pm 20$  kOe and an isomer shift of  $0.25 \pm 0.04$  mm/s (relative to 310 ESS) against a background of a paramagnetic line with the same isomer shift. The values of the hf field and the isomer shift are intermediate between that for  $\text{Fe}^{3+}$  and  $\text{Fe}^{\text{IV}}$ . These observations lead us to believe that the Mössbauer probe sees a chemical environment in between that of  $\text{Fe}^{3+}$  and  $\text{Fe}^{\text{IV}}$ . A similar situation has been reported for magnetite by Ito, Ono and Ishikawa [9]. The observation of hf spectra only above  $x > 0.125$  is marked by a change in the paramagnetic Curie temperature  $\theta$  from a negative value to a positive value and a break in the rhombohedral angle  $\alpha_R$  and the hexagonal  $c$  axis at  $x = 0.125$ . All the compositions except  $x = 0.5$  show a slightly rhombohedral distortion.

3.4 Above the respective Curie temperatures (for  $x > 0.125$ ) which agree remarkably well with the Curie temperature determined by gross magnetization experiments [10, 11], these compositions give a single line with an isomer shift corresponding to a chemical state in between  $\text{Fe}^{3+}$  and  $\text{Fe}^{\text{IV}}$ .

3.5 The compositions  $0.125 < x \leq 0.5$  exhibit a paramagnetic peak as well as a ferromagnetically split spectrum below  $T_c$ . The area under the paramagnetic peak relative to the area under the ferromagnetic peaks increases with decreasing  $x$  and with increasing temperatures. The compositions have ferromagnetic pockets in a paramagnetic matrix ; the ferromagnetic particle size decreasing with decreasing  $x$ .

3.6 The existence of a sharp cut off in the reflectivity vs. energy curve for  $x > 0.2$  indicates itinerant carriers with relatively high mobility. This observation is supported by the value of and temperature coefficient of resistivity and Seebeck coefficient. It is significant to note that both the electrical conductivity and the

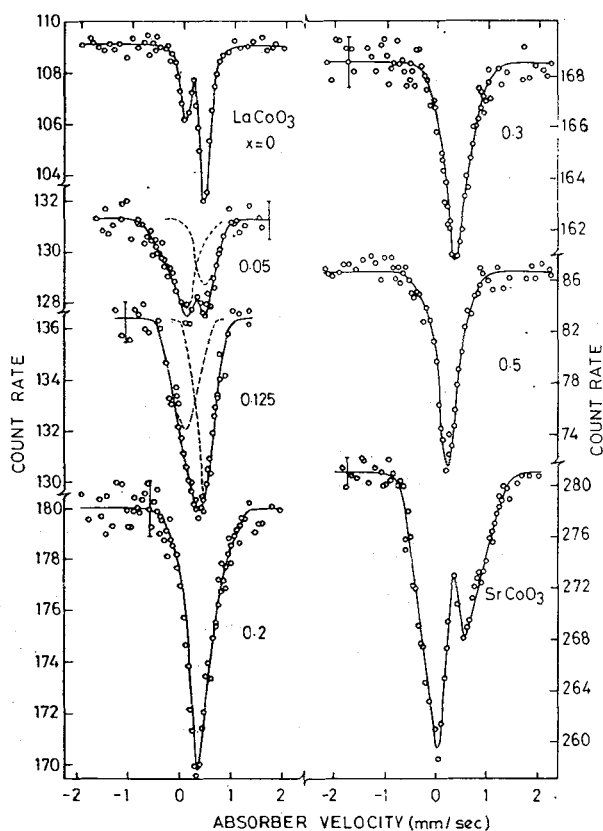


FIG. 1. — Typical Mössbauer spectra of  $\text{LaCoO}_3$ ,  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  ( $0 < x \leq 0.5$ ) and nominal  $\text{SrCoO}_3$  sources at room temperature when matched against  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  single crystal absorbers.

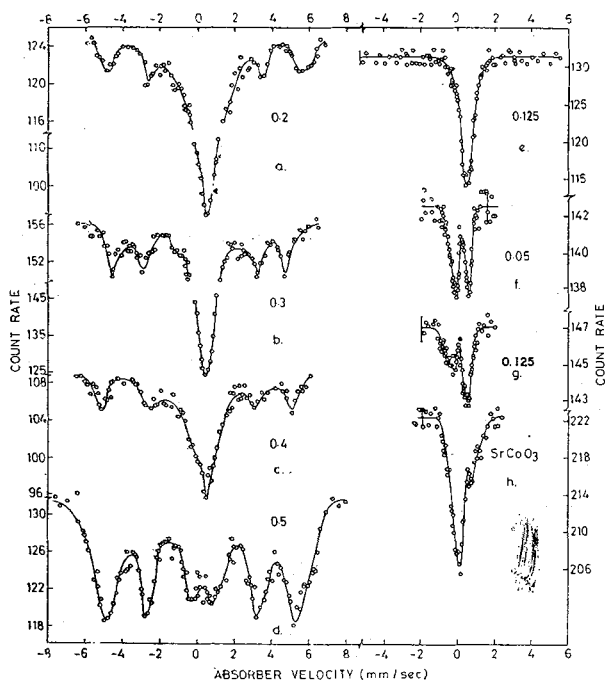


FIG. 2. — Mössbauer spectra for various compositions at 78 K. a-e) matched against 310 ESS absorber; f-h) matched against  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  absorber.

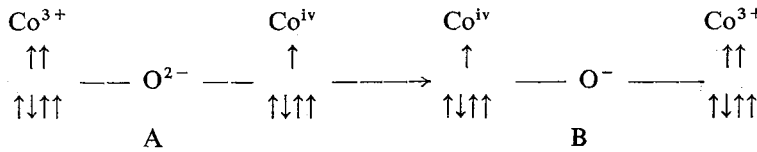
Seebeck coefficient vary continuously through the ferromagnetic transition temperature  $T_c$ .

The ferromagnetism observed in the system  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  could be due to one of the three mechanisms, namely : (1) ordering of high spin  $\text{Co}^{3+}$  and low spin  $\text{Co}^{IV}$  cations through ferromagnetic superexchange in between them via the intervening oxygen ions [5, 6] (2) Zener double exchange [12] and (3) itinerant electron ferromagnetism [10, 13].

The first mechanism based on localized electron model due to Anderson was modified by Goodenough to account for the ferromagnetic interaction observed in this system. He showed that if octahedral site magnetic cations are located on opposite sites of a common anion, they interact ferromagnetically if one cation has completely empty  $e_g$  orbitals and the other has half filled  $e_g$  orbitals. On the postulated existence of  $\text{Co}^{3+}$  and  $\text{Co}^{IV}$  he explained ferromagnetism in

$\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  ( $x > 0.125$ ). However, later on, this mechanism was abandoned in favour of the itinerant electron ferromagnetism for the reasons indicated in the introduction. The present Mössbauer, electrical conductivity and other studies provide stronger evidence for abandoning the mechanism based on localized electrons.

One of the conditions to be satisfied for the Zener mechanism to operate is the existence of cations carrying charges differing by unity and occupying equivalent positions. According to Zener, the interaction is brought about by the simultaneous transfer of an electron from oxygen 2p orbital to the tetravalent cobalt and from trivalent cobalt to the 2p orbital of oxygen—a so-called double exchange. Indeed in this double exchange process, a 3d hole associated with  $\text{Co}^{IV}$  is effectively transferred to the trivalent cobalt ion. The unit process would involve a change from configuration A to the configuration B :



If the relaxation time between  $\text{Co}^{3+} \rightleftharpoons \text{Co}^{IV}$  transformation  $\tau_R$  is less than the Larmour precession time  $\tau_L$  corresponding to the hf field at the site, then one would observe a single set of six finger pattern with an hf field and isomer shift in between that of  $\text{Fe}^{3+}$  and  $\text{Fe}^{IV}$ . Conversely if  $\tau_R > \tau_L$  then one should observe two distinct sets of six finger patterns with hf field characteristic of  $\text{Fe}^{3+}$  and  $\text{Fe}^{IV}$ . The observation of one set of six finger pattern with an isomer shift and hf field in between that for  $\text{Fe}^{3+}$  and  $\text{Fe}^{IV}$  would tend to support Zener mechanism with the relaxation time  $\tau_R < \tau_L$ . Although Mössbauer studies of the system below  $T_c$  can be explained on the basis of Zener double exchange mechanism, there are several other observations which unambiguously show that the Zener mechanism is not operative. Thus if Zener mechanism were involved, there should have been a break in the electrical conductivity at  $T_c$  either because of the formation of magnetic polaron or critical scattering in the vicinity of  $T_c$ . Experimental evidence is unambiguous in that there is no discontinuity either in electrical conductivity or Seebeck coefficient. Further, the observation of a single Mössbauer line above  $T_c$  with an isomer shift in between that for  $\text{Fe}^{3+}$  and  $\text{Fe}^{IV}$  indicates that electrons are itinerant above the Curie temperature as well.

It is possible to harmonize Mössbauer studies and electrical measurements only on the basis of itinerant electron ferromagnetism. The itinerant electron model proposed by Goodenough [10, 13] is summarised in figure 3, which shows schematically the cobalt 3d

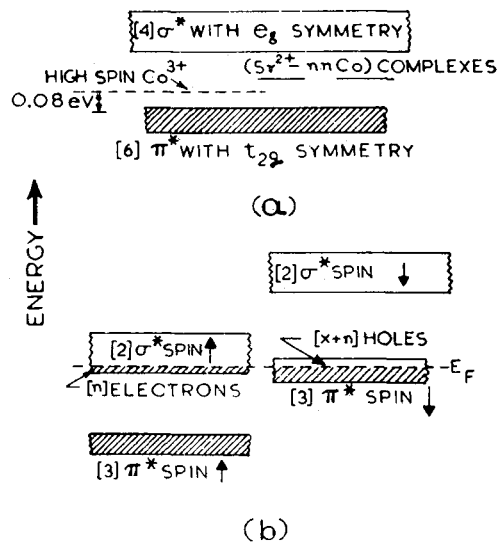


FIG. 3. — a) Cobalt 3d bands for La-rich region showing the  $\text{Sr}^{2+}$  impurity level; b) Cobalt 3d bands for ferromagnetic  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  if no correlation splitting of  $\pi^*$  bands (after Goodenough, ref. [10]).

bands for small and large  $x$ . At  $T = 0 \text{ K}$  and small  $x$ , a narrow  $\pi^*$  band (formed from the crystal field d orbitals of  $t_{2g}$  symmetry) is filled. The cobalt atoms nearest neighbour to  $\text{Sr}^{2+}$  ion provide molecular d orbitals, those formed from atomic  $t_{2g}$  or  $e_g$  orbitals having about the same deep acceptor energy level. Thermal excitation to the high spin  $\text{Co}^{3+} : t_{2g}^4 e_g^2$

configuration creates a magnetic ion, but it does not produce a mobile hole. Mobile holes are created by excitation of an electron from the  $\pi^*$  band to an acceptor level. At higher  $\text{Sr}^{2+}$  concentrations, the acceptor orbitals interact to form an impurity band. Because the high spin  $\text{Co}^{3+}$  and low spin  $\text{Co}^{4+}$  configurations have comparable energies, the formation of impurity bands generates spontaneous ferromagnetism having the  $\sigma^*$  bands of upspin overlapping the  $\pi^*$  bands of down spin. Because, there is a critical  $\text{Sr}^{2+}$  ion concentration for impurity band formation which from experiments is  $x_c = 0.125$ , chemical inhomogeneities can produce interpenetrating ferromagnetic and paramagnetic domains. On this model, the paramagnetic component is expected to decrease with increasing  $x$  and decreasing  $T$  as has indeed been observed. So long as  $\sigma^*$  band remains less than one quarter filled and the  $\pi^*$  band more than three quarters filled, itinerant electron ferromagnetism having Weiss constant  $\theta > T_c$  is to be anticipated. For  $x < 0.1$  where figure 3a applies, one should expect two distinct valence states of cobalt  $\text{Co}^{3+}$  and  $\text{Sr}^{2+}$  impurity associated tetravalent cobalt along with  $\text{Co}^{11}$  which is normally present in  $\text{LaCoO}_3$ . In conformity with this expectation, the Mössbauer spectra for this composition range show two distinct

peaks, the lower velocity resonance corresponding to low spin ions (low spin trivalent iron and tetravalent iron with  $\text{Sr}^{2+}$  impurity association) and a higher velocity resonance arising out of high spin trivalent  $\text{Fe}^{3+}$  (arising out of high spin  $\text{Co}^{3+}$ ). So long as the  $\text{Sr}^{2+}$  ions are isolated, the ground acceptor states appear to be doublets formed from  $t_{2g}$  orbitals of the  $\pi^*$  band. However, with increase in  $x$ , interaction between  $\text{Sr}^{2+}$  ion impurity centres takes place leading to the formation of an impurity band and an initiation of itinerant electron ferromagnetism in small pockets essentially in the  $\text{Sr}^{2+}$  rich regions. With further increase in  $x$ , the ferromagnetic particle size increases and the description of figure 3b is valid. In the itinerant electron ferromagnetic portion, the cobalt ion has a time averaged environment in between that characteristic of high spin trivalent cobalt and low spin tetravalent cobalt. This description predicts that in the neighbourhood of critical concentration  $x_c = 0.125$ , the matrix could be adequately described as paramagnetic. With few ferromagnetic particles, whereas for higher values of  $x$  reaching 0.5, the matrix is essentially ferromagnetic and metallic with small pockets of paramagnetic particles. The Mössbauer results exactly reproduce what is expected on the basis itinerant electron ferromagnetism.

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