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FAST TRACK COMMUNICATION

The electronic structure of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ thin films and its T_c dependence as studied using angle-resolved photoemission

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Abstract

We present angle-resolved photoemission spectroscopy (ARPES) results for thin films of the three-dimensional manganese perovskite $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. We show that the temperature of the transition (T_c) from the paramagnetic insulating to the ferromagnetic metallic state is closely related to details of the electronic structure, particularly to the spectral weight at the \mathbf{k} -point, where the sharpest step at the Fermi level was observed. We found that this \mathbf{k} -point is the same for all the samples, despite their different values of T_c . The change of T_c is discussed in terms of kinetic energy optimization. Our ARPES results suggest that the change of the electronic structure for the samples having different transition temperatures is different from the rigid band shift.

(Some figures in this article are in colour only in the electronic version)

Colossal magnetoresistance (CMR) in hole-doped manganese oxides with perovskite structures [1, 2] is a phenomenon of great scientific and technological importance. For a certain range of doping, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO) shows a large decrease in resistivity upon cooling, associated with a paramagnetic (PM) to ferromagnetic (FM) transition [3, 4]. Close to the transition temperature T_c , the resistivity can be further strongly reduced by applying a magnetic field, in a phenomenon known as colossal magnetoresistance. The temperature-dependent resistivity in the FM phase has been qualitatively explained by the double-exchange (DE) mechanism [5, 6]. The premise is as follows: in the FM phase, LSMO contains mixed-valent Mn^{3+} and Mn^{4+} . For the site-symmetry of the cation in the MnO_6 octahedra, the

valence states in question are $\text{Mn}^{4+}:t_{2g}^3$ and $\text{Mn}^{3+}:t_{2g}^3 e_g^1$. There are $(1-x)e_g$ electrons per unit cell, which are free to move through the crystal, subject to a strong Hund's coupling to the localized Mn^{4+} ($S = 3/2$) spins. The kinetic (band) energy is minimized by making all the spins parallel. It was also realized that the DE alone is not enough to explain CMR and other effects, especially the insulator-like transition above T_c . The DE framework should be supplemented with more refined ideas (e.g. Jahn–Teller distortions, polaron formations) [7]. Among the Ruddelston–Popper series of manganites, $(\text{La}, \text{Sr})_{n+1}\text{Mn}_n\text{O}_{3n+1}$ ($n = 1, 2, \dots$), $(\text{La}, \text{Sr})\text{MnO}_3$ has the highest T_c and its resistivity at low temperatures is about two orders of magnitude lower than that of the layered manganite ($n = 2$) [8].

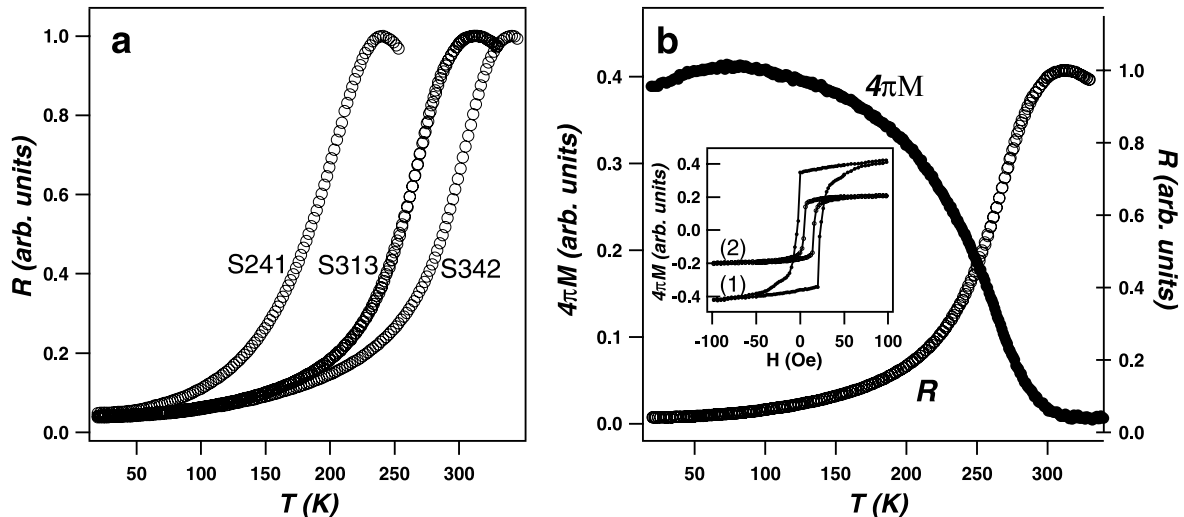


Figure 1. (a) Resistance versus temperature for samples S241, S342 and S313. The resistance was normalized to the peak value. (b) Resistance and DC magnetization of S313 versus temperature. Inset: magnetic hysteresis curves of S313 measured at temperatures 100 K (1) and 250 K (2).

One major obstacle in understanding the physics of the three-dimensional manganites has been a lack of detailed knowledge of the electronic structure of the low binding energy electronic states. So far, only very limited experimental results on \mathbf{k} -resolved electronic structures of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ have been reported [9–11]. In this work we apply angle-resolved photoemission spectroscopy (ARPES) to probe the electronic structure of metallic single crystalline films of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ with different T_c . We observe that the finite spectral weight at the Fermi level (E_F) is closely associated with a broad peak which disperses at higher binding energies. The difference in T_c is directly reflected by a change in the electronic structure of the lowest binding energy states.

1300 Å-thick single crystalline thin films of LSMO were prepared by *in situ* heteroepitaxial growth on SrTiO_3 (001) substrates by a novel adaptation of pulsed laser deposition [12, 13]. *In situ* reflection high-energy electron-diffraction patterns and Kiessig fringes in *ex situ* x-ray reflectivity curves demonstrate that the films have a surface roughness of less than one monolayer. Low-energy electron-diffraction analysis shows a clear (1×1) pattern with no sign of surface reconstruction. Three LSMO samples with ascending Sr/La ratios (0.44, 0.48, 0.52) were prepared. Because the hole-doping level could be changed by the small variation of the oxygen stoichiometry, which can result in a change of T_c , we further characterize the bulk properties of the samples by transport measurements. Figure 1(a) shows the resistance–temperature curves [$R(T)$] obtained from four-probe measurements. The transition temperatures determined from these data are 241 K, 342 K and 313 K, respectively. In the rest of the paper we will label the samples by their T_c as S241, S342 and S313, respectively. The transition temperatures were confirmed by DC magnetization measurements. Figure 1(b) shows the magnetic momentum [$4\pi M(T)$] of S313, together with $R(T)$, as a function of temperature. The stoichiometry of S313, as determined by

ex situ using Rutherford backscattering spectrometry, was $\text{La}_{0.66}\text{Sr}_{0.34}\text{MnO}_3$.

ARPES measurements were performed at the surface and interface spectroscopy (SIS) beamline at the Swiss light source (SLS). During measurements, the pressure always remained less than 1×10^{-10} mbar. The spectra were recorded with a Scienta 2002 analyzer with an angular resolution of better than 0.2° . The energy resolution was relaxed to 40 meV to obtain a high intensity. All measurements were performed at temperature below 30 K. The reduced zone scheme is used to indicate the wavevectors (\mathbf{k}) in reciprocal space. The free-electron final state approximation with $(V_0 - \phi) = 10.16$ eV [9] is applied to determine paths or \mathbf{k} -points, where V_0 is the inner potential and ϕ is the work function. Photon energies (E_{hv}) are indicated in the figure captions. In our ARPES measurements the polar angles (between the surface normal and the direction of the outgoing photoelectrons) were in the range of $-5^\circ < \theta < 18^\circ$.

We show representative ARPES spectra taken from S313 in figure 2. Similar ARPES spectra were also obtained for S241 and S342. The spectra were collected along paths parallel to the sample surface in the (010) mirror plane (figure 2(a)) and $(1\bar{1}0)$ mirror plane (figure 2(b)), with linearly horizontally polarized light and with circularly polarized light, respectively. The common features in figures 2(a) and (b) are: close to the (001) axis a broad peak (peak A) sits on the sloped background and shows nearly no dispersion along k_{\parallel} (the component of \mathbf{k} parallel to sample surface). Away from the (001) axis at about $k_{\parallel} = 0.3\pi/a$, another peak (peak B) appears at higher binding energy and disperses towards E_F as k_{\parallel} increases. Further increasing k_{\parallel} does not change the peak position of peak B in the (010) mirror plane, while it folds back to high binding energy in $(1\bar{1}0)$ mirror plane (not shown). The bandwidth of peak B in the $(1\bar{1}0)$ mirror plane is larger than that in the (010) mirror plane. In contrast to its non-dispersive behavior with respect to k_{\parallel} in the vicinity of the (001) axis, peak A does show a dispersion with respect to k_{\perp} (along the surface

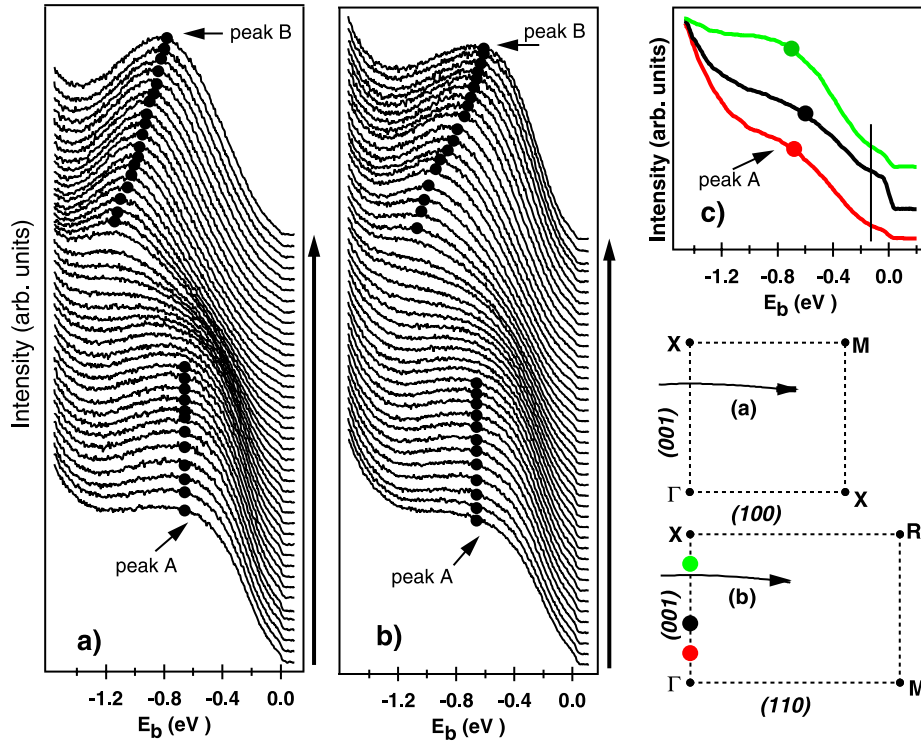


Figure 2. ARPES spectra for S313 at 30 K. (100) and (110) are along the sample surface, while (001) is the surface normal. Peak A and peak B are used to facilitate the discussion in the text. (a) and (b) EDCs taken by using $E_{h\nu} = 44$ eV with linearly horizontally polarized light and with circularly polarized light, respectively. The paths in the BZ are indicated with arrowed lines in the middle and bottom-right of the figure. Circles indicate the peak positions of broad peaks. (c) EDCs taken with circularly polarized light with $E_{h\nu} = 34$ eV (lower), 38 eV (middle) and 46 eV (upper) in the normal emission. The k -points are indicated in the bottom-right of the figure with filled circles for $E_{h\nu} = 34$ eV (lower), 38 eV (middle) and 46 eV (upper), respectively. The vertical line indicates the energy where the slopes of the EDCs change, circles indicate the peak positions of broad peaks.

normal, figure 2(c)). It can be seen that there is a close correlation between the peak position and the spectral weight at E_F . Specifically, when peak A approaches E_F , the spectral weight at E_F increases and the step at E_F sharpens. It should be noted that a finite spectral weight at E_F has only been observed in the vicinity of the (001) axis in the Brillouin zone (BZ) with $k_{\parallel} < 0.4\pi/a$. The highest spectral weight and the sharpest step at E_F have been found at $k \approx (0, 0, 0.4)\pi/a$, when $E_{h\nu} = 38$ or 67 eV is used. This applies for all the investigated samples, despite their different T_c . Peak B also disperses along a path parallel to the (001) axis [9]. This is strong circumstantial evidence that the dispersion of peak B derives from the bulk electronic structure. However, the dispersive feature is much weaker than that in the planes perpendicular to the (001) axis. It is important to mention that we have traced the peak B in different mirror planes, as well as many general k -points in the BZ by using various photon energies and photon polarizations. We found that there is a correspondence between the positions of peak B and the T_c of the samples (figure 3(c)): the higher T_c is, the closer becomes peak B to E_F . However, for all three samples, the centroids of peak B never approach closer than 0.6 eV to E_F , and there is never more than a vanishingly small spectral weight at E_F .

Besides the many similarities, there are some quantitative differences in the ARPES spectra of S241, S342 and S313. Figures 3(a) and (b) show the EDCs taken with $E_{h\nu} = 38$ eV,

corresponding to $k \approx (0, 0, 0.4)\pi/a$, where the highest spectral weight at E_F was observed for all three samples. The spectra were normalized to the total areas under the EDCs. An important observation is that the spectral weight at E_F is closely related to the transition temperatures, namely, the spectral weight at E_F is higher when T_c increases (figure 3(a)). In order to remove any ambiguity when comparing the spectral weight at E_F , two additional normalization methods were employed. First, to minimize the contribution of the sloped background, we normalized the EDCs to the intensity at $E_B = 200$ meV below E_F (the inset of figure 3(a)). Second, for normalization we used the ‘shoulder’ of the Mn t_{2g} states of Mn (figure 3(b)). In both cases the spectral weights at E_F for different samples have the same trend as the T_c s of the samples. Figure 3(a) also shows that the line shape of peak A changes dramatically for the samples with different T_c . For S241, it has the lowest T_c among the three samples, and peak A is well defined. As T_c increases some spectral weight is transferred from high binding energies to that close to E_F , and at the same time peak A becomes broader and less pronounced. On the other hand, the line shape of peak B is rigid with respect to the change of T_c . Figure 3(c) shows the EDCs for S241 and S313 taken at the same $k \approx (0.6, 0, 0.7)\pi/a$ where a single e_g band is expected [14, 15]. The peak position of the EDC of S313 is shifted about 170 meV towards E_F with respect to that of S241. After offsetting the EDC of S313 by -170 meV the two EDCs overlap over nearly the entire energy range, except at the very

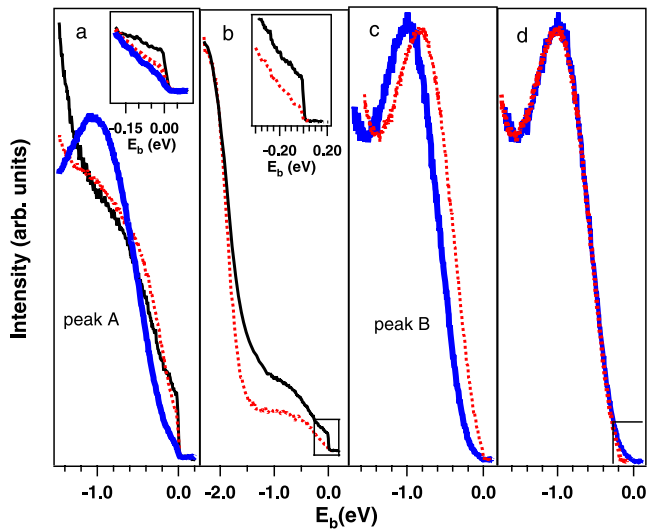


Figure 3. EDCs for S241 (thick solid), S342 (thin solid) and S313 (dotted). (a) EDCs at $k \approx (0, 0, 0.4)\pi/a$ taken with $E_{hv} = 38$ eV, normalized to the total area under EDCs. In the inset spectra were normalized to the intensity at $E_b = -200$ meV. (b) EDCs for S342 and S313 at $k = (0, 0, 0.4)\pi/a$. The inset is a magnification of the marked box. Spectra were normalized to the highest E_b shown in the figure. (c) EDCs for S241 (taken with $E_{hv} = 101$ eV) and S313 (taken with $E_{hv} = 45$ eV) at $k \approx (0.6, 0, 0.7)\pi/a$. (d) The same as (c) with the EDC of S313 offset by -170 meV. The labels of peak A and peak B follow the peak assignments introduced in figure 2.

low binding energy tail, where the EDC of S313 has a smaller spectral weight (the marked box in figure 3(d)).

We now address the issue of coherent electronic excitations at low binding energies. In recent ARPES studies of the layered manganite $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ with $x \approx 0.4$, it has been shown that quasiparticle peaks do exist close to the Fermi level [16–18]. The quasiparticle peaks are followed by incoherent excitations, and the single particle spectral function has a ‘peak-dip-hump’ structure which indicates strong many-body effects and/or electron–lattice coupling. As our samples are three-dimensional, one would expect a higher spectral weight of coherent electronic excitations in the energy range where quasiparticles were observed in the layered manganite. The absence of sharp excitations in our ARPES spectra may be explained by the uncertainty of k_{\perp} , the component of \mathbf{k} along the surface normal, in the photoemission process. Because k_{\perp} is not conserved, due to the breaking of the translational symmetry at the sample surface, ARPES spectra in a three-dimensional system will be broadened (Δk_{\perp}), especially for an energy band that has a large dispersion in the direction along the surface normal. The large change of the slopes as marked by the vertical line in figure 2(c) may indicate that the peak-dip-hump structure also exists in our samples. However, the broadening effect smears out the dip in the ARPES spectra.

We observed the finite spectral weight at E_F only in the vicinity of $(0, 0, 0.4)\pi/a$ in the \mathbf{k} -space. This particular \mathbf{k} -point would correspond to the \mathbf{k}_F of the electron-pocket centered at Γ point from band structure calculations [14, 15] when assuming that $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ has a cubic structure. However, in our measurements there is never more than a vanishingly small spectral weight at E_F at equivalent \mathbf{k} -points

$(0.4, 0, 0)\pi/a$ or $(0, 0.4, 0)\pi/a$, despite that various photon polarizations and different photon energies corresponding to the same \mathbf{k} -points in the reduced zone scheme were used in our experiments. Finite spectral intensities at the predicted Fermi surface of the hole-pocket centered at the R point (the corner of the BZ) in those calculations was also not observed in our measurements, and indeed was not reported in other ARPES studies on the same system [11]. As the calculated Fermi surface of the hole-pocket has a cubic-like shape [14, 15], the nesting of the Fermi surface between the parallel faces of the cube may introduce an instability and result in a gap opening in the electronic excitation spectra. The consequence of this will be that the spectral weight at E_F diminishes and the relevant energy band folds back from E_F . In our previous ARPES studies on LSMO we observed the folding back of an energy band which is supposed to cross the calculated Fermi surface of the hole-pocket (see figures 1(a) and 2(a) in [10]). Another possibility to explain the absence of the hole-pocket is heteroepitaxial strain in the samples. The common point in our ARPES studies and others is that single crystalline LSMO films grown on SrTiO_3 substrates were used in the experiments. The tensile stress due to the lattice mismatch between the LSMO and the substrate results in the ratio between the lattice constant in the [001] direction and those in the equivalent [100] directions is less than unity. Further studies are needed to understand the discrepancy between the experimental and calculated results, namely, is it due to the nesting, the change of lattice constant, a combination of these, or other effects? To clarify the role played by the strain induced by any lattice mismatch, it will be very useful to perform ARPES measurements on single crystals grown on different substrates, e.g. NdGaO_3 . In this case the compressive stress results in the lattice constant in [001] direction being larger than that in [100] direction. Comparison of the ARPES results on LSMO crystals under different stress will be very important in understanding how the electronic structure responds to small changes of the lattice constants.

Our ARPES results also indicate that the change of the electronic structure for the samples with different T_c is different than the rigid band shift, as suggested in the angle integrated photoemission on the LSMO films [19]. This is manifested by the facts that (a) for all the samples, the highest spectral weight was found at the same \mathbf{k} -point $(0, 0, 0.4)\pi/a$ when $E_{hv} = 38$ eV is used in the measurements; (b) the centroid of peak A of S313 is closer to E_F than that of S342 at this \mathbf{k} -point, but S313 has a lower spectral weight at E_F than S342 (figure 3(a)), which is opposite to what one would expect from the rigid band picture [20]; and (c) for S241 the peak position of peak A at $k \approx (0, 0, 0.4)\pi/a$ is about the same as that of peak B at $k \approx (0.6, 0, 0.7)\pi/a$ (figures 3(a) and (c)). When going to S313, the shift of the peak position of peak B (170 meV) is much smaller than that of peak A, ~ 500 meV, and compared to the small change in the line shape of the peak B at the low binding energy tail (the marked box in the figure 3(d)) the spectral weight of peak A undergoes a large redistribution (figure 3(a)).

The relationship between T_c and the spectral weight at E_F , namely that a higher T_c is associated with more spectral weight

at E_F , can be qualitatively explained by the double-exchange model [21–23]. The essential quantity for the transition from PM to FM is the metallic density of charge carriers, which are subject to Hund's rule and other interactions. The scale of the transition temperature is set by the kinetic energy of the mobile charge carriers, which is proportional to the expectation value of the hopping Hamiltonian. The highest T_c is obtained when the kinetic energy is maximized in the system. As the Fermi level divides the occupied states and unoccupied states of electrons, the spectral weight in electronic excitation spectra is directly related to the hopping probability given by the number of electrons that are free to move from site to site and the number of available empty states that the electrons can hop into.

In summary, our ARPES measurements on LSMO thin films with different T_c reveal both common features and quantitative differences in their electronic structures in the FM phase. It was found that T_c is closely related to the spectral weight at E_F at $\mathbf{k} \approx (0, 0, 0.4)\pi/a$, where the sharpest step at E_F was observed for all investigated samples. We also provide evidence that the rigid band picture cannot account for the change of the electronic structure for the samples having different T_c resulting from the change of dopings.

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References

- [1] Kusters R M *et al* 1989 *Physica B* **155** 362
- [2] Jin S *et al* 1994 *Science* **264** 413
- [3] Urushibara A *et al* 1995 *Phys. Rev. B* **51** 14103
- [4] Hemberger J *et al* 2002 *Phys. Rev. B* **66** 094410
- [5] Zener C 1951 *Phys. Rev.* **82** 403
- [6] Cieplak M 1978 *Phys. Rev. B* **18** 3470
- [7] Millis A J *et al* 1995 *Phys. Rev. Lett.* **74** 5144
- [8] Kimura T *et al* 1998 *Science and Technology of Magnetic Oxides (Mater. Res. Soc. Symp. Proc. vol 494)* ed M F Hundley, J H Nickel, R Ramesh and Y Tokura (Warrendale, Pennsylvania: Materials Research Society) p 347
- [9] Shi M *et al* 2004 *Phys. Rev. B* **70** R140407
- [10] Falub M C *et al* 2005 *Phys. Rev. B* **72** 054444
- [11] Chikamatsu A *et al* 2006 *Phys. Rev. B* **73** 195105
- [12] Willmott P R and Huber J R 2000 *Rev. Mod. Phys.* **72** 315
- [13] Willmott P R, Herger R and Schleputz C M 2004 *Thin Solid Films* **453/454** 438
- [14] Livesay E A *et al* 1999 *J. Phys.: Condens. Matter* **11** L279
- [15] Pickett W E and Singh D J 1997 *Phys. Rev. B* **55** R8642
- [16] Sun Z *et al* 2006 *Phys. Rev. Lett.* **97** 056401
- [17] Mannella N *et al* 2005 *Nature* **438** 474
- [18] de Jong S *et al* 2007 *Preprint* **0710.2054**
- [19] Horiba K *et al* 2005 *Phys. Rev. B* **71** 155420
- [20] Shen K M *et al* 2004 *Phys. Rev. Lett.* **93** 267002
- [21] Kubo K and Ohata A 1972 *J. Phys. Soc. Japan* **33** 21
- [22] Ohata N 1973 *J. Phys. Soc. Japan* **34** 343
- [23] Millis A J 2000 *Colossal Magnetoresistive Oxides* ed Y Tohura (Amsterdam: Gordon and Breach) p 53