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Influence of high-energy electron irradiation on the transport properties of $La_{1-x}Ca_xMnO_3$ films ($x \approx 1/3$)

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Abstract. The effect of crystal lattice disorder on the conductivity and colossal magnetoresistance in $La_{1-x}Ca_xMnO_3$ ($x \approx 0.33$) films has been examined. The lattice defects are introduced by irradiating the film with high-energy ($\simeq 6$ MeV) electrons with a maximal fluence of about 2×10^{17} cm^{-2}. This comparatively low dose of irradiation produces rather small radiation damage in the films. The number of displacements per atom (dpa) in the irradiated sample is about 10^{-5}. Nevertheless, this results in an appreciable increase in the film resistivity. The percentage of the resistivity increase in the ferromagnetic metallic state (below the Curie temperature T_c) was much greater than that observed in the insulating state (above T_c). At the same time irradiation has much less effect on T_c or on the magnitude of the colossal magnetoresistance. A possible explanation of such behavior is proposed.

PACS. 75.30.Vn Colossal magnetoresistance – 72.80.Ga Transition-metal compounds – 72.60.+g Mixed conductivity and conductivity transitions

1 Introduction

In recent years considerable attention has been focussed on the structural, magnetic and electron transport properties of perovskite oxides of the type $R_{1-x}A_xMnO_3$ (where R is a rare-earth element, A a divalent alkaline-earth element). This interest was caused by observation of an extremely large negative magnetoresistance in these compounds [1,2], which was called colossal magnetoresistance (CMR). Along with fundamental importance for condensed matter physics, this phenomenon also offers applications in advanced technology. Therefore the problem of CMR continues to be topical.

The doped manganites undergo a phase transition with decreasing temperature from a paramagnetic insulating state into a highly conducting ferromagnetic phase. It can be said that this insulator-metal transition occurs approximately simultaneously with a paramagnetic-ferromagnetic transition (at least in good quality crystals). The external magnetic field shifts the transition temperature T_c (which is usually near room temperature in well-ordered samples with $x \approx 0.33$) to higher temperature producing the CMR (see reviews in Refs. [3–6]).

The most pronounced CMR effect was found in $La_{1-x}Ca_xMnO_3$ films with $x \simeq 1/3$. The undoped compounds from this series ($LaMnO_3$ and $CaMnO_3$) are antiferromagnetic insulators. In the intermediate range of doping ($0.2 < x < 0.4$) $La_{1-x}Ca_xMnO_3$ is a ferromagnetic conductor at low temperature. The ferromagnetic state is believed to be due to the appearance of Mn^{4+} ions with substitution of La^{3+} by a divalent cation. It can be assumed that ferromagnetism results from the strong ferromagnetic exchange between Mn^{3+} and Mn^{4+}. The appearance of such an interaction can be qualitatively explained within the double-exchange (DE) model [7–9]. This model, however, cannot alone explain either the huge drop in resistance at the transition, or the real nature of the insulating state at $T > T_c$ and, therefore, the conductivity mechanism in this state. Thus, additional physical processes have been invoked to explain the insulating state and insulator-metal transition. Among them are lattice (polaron) effects [10] and the possibility of phase separation into charge-carrier-poor and charge-carrier-rich regions [3,6,11].

The conductivity of $La_{1-x}Ca_xMnO_3$ with $x < 0.5$ is determined by holes which appear as the result of replacement of trivalent La by divalent atoms. The DE model is based on the assumption that the holes in doped manganites correspond to Mn^{4+} ions arising among the regular Mn^{3+} ions due to doping. However another point of view exists [3,6,12] that the holes go on oxygen sites. The experimental data on this point are contradictory. There is experimental evidence (see Ref. [13] and references therein) that holes doped into $LaMnO_3$ are mainly

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of Mn d character. On the other hand experimental studies described in references [14,15] give evidence that the charge carriers responsible for conduction in doped manganites have significant oxygen $2p$ character. This is just one example illustrating that to date there is no consensus in the scientific community about the basic transport properties of doped manganites. It may be inferred, therefore, that the understanding of these properties is far from completion and that further experimental and theoretical investigations of this matter are necessary.

It is well-known that doped manganites of the same chemical composition but with different degrees of crystal lattice disorder show quite different transport and magnetic properties. The disorder can be altered either with variation of sample preparation conditions (for example, substrate temperature and post-annealing at film preparation) or using radiation damage [16–19]. With increasing disorder the resistivity peak temperature $T_{\rm p}$ and the Curie temperature $T_{\rm c}$ decrease, while the magnetoresistance increases. In understanding the nature of CMR the influence of disorder of the crystal lattice is one of the important points and should be taken into account together with spin, lattice and other effects. This communication is concerned mainly with this problem.

The object of investigation was $La_{1-x}Ca_xMnO_3$ thinfilms with $x \approx 1/3$. The disorder was enhanced by irradiating the films at room temperature with high-energy ($\simeq$ 6 MeV) electrons. This high energy of the incident electrons makes it possible to produce a uniform distribution of damage defects, without any significant variation of defect concentration as a function of depth (all incident electrons go through the film). In contrast to low energy ion irradiation, no interstitial implanted impurity ions can remain in the film for electron irradiation to produce inhomogeneity. Similarly, in contrast to very high energy ion irradiation, electron irradiation in our study does not produce extended defects, such as cascades and clusters. This facilitates the interpretation of the experimental results. At the low damage level in this experiment, however, the electron radiation damage may indeed be quite similar to damage induced by very low level, intermediately high-energy ion irradiation.

The maximal electron fluence in this study was about 2×10^{17} cm^{-2}. The calculated quantity of displacements per atom (dpa) is about 10^{-5}. This comparatively small radiation damage results in an appreciable increase in film resistivity. It was found that the relative resistivity increase in the ferromagnetic metallic state (below Curie temperature $T_{\rm c}$) was much greater than in the insulating state (above $T_{\rm c}$). Such a small amount of radiation damage should not induce any noticeable resistance variations in ordinary ferromagnetic or non-ferromagnetic metals. At the same time any large influence of electron irradiation with the above-mentioned fluence on the $T_{\rm c}$ and the magnitude of the colossal magnetoresistance was not observed. Possible reasons for this unusual behavior for the doped manganites are discussed.

2 Experiment and results

The $La_{1-x}Ca_xMnO_3$ films were prepared by physical vapor codeposition of La, Ca and Mn from three separate, independently controlled sources, similar to the technique for preparation of Ca-Ba-Cu oxide precursors for growth of oriented $Tl_2Ca_2Ba_2Cu_3O$ thin films [20]. The deposition was performed in 10^{-5} Torr of oxygen onto $LaAlO_3$ substrates heated to about 600 °C. La and Mn were evaporated from alumina crucibles heated with a tungsten filament, and Ca was evaporated from a Knudsen cell. Post deposition anneals of the films at 900 °C in flowing oxygen improved the CMR behavior and produced well-ordered films. The composition of the film was determined by microprobe analysis of an unannealed film deposited simultaneously onto a fused quartz substrate. The films were also characterized by X-ray diffraction and AC susceptibility measurements. Agreement among the values of $T_{\rm c}$ determined by the real part χ' of the susceptibility and $T_{\rm p}$ determined by both measurements of the resistivity and the imaginary part χ'' of the susceptibility confirm that the films have good chemical and magnetic homogeneity based on the scheme proposed by Araujo-Moreira *et al.* [21]. Further details of the preparation technique and characterization are presented elsewhere [22].

Although a sensitive magnetometer was not available for magnetization measurements with these films, AC susceptibility was measured, both for unirradiated and irradiated films. In each case the onset of the sharp increase in the real part of the susceptibility χ' and the sharp peak in the imaginary part of the susceptibility χ'' coincide within experimental error with the value of $T_{\rm p}$. The sharp increase in the low frequency χ' ($\approx$ 140 Hz) data presumably corresponds to the magnetic transition temperature $T_{\rm c}$. Representative data for an unirradiated film is presented in Figure 4 of reference [22]. Data for χ' and χ'' for one of the films irradiated in this study (not shown) has much less noise and provides clear evidence that $T_{\rm c}$ and $T_{\rm p}$ coincide, both for the unirradiated and irradiated films in this study. This is not unexpected, however, since ion irradiation studies have shown [18] that for high quality films with small lattice damage, these two temperatures are essentially the same, but for much higher lattice damage $T_{\rm p}$ will be at much lower temperature than $T_{\rm c}$. Throughout this paper reference will be made to $T_{\rm p}$, but, since $T_{\rm p}$ and $T_{\rm c}$ are essentially identical, the conclusion from these experiments apply to both equally well.

During the electron irradiation the films were in a special holder which was cooled with running water and a powerful fan. The estimated overheating above room temperature during the irradiation was no more than $\simeq$ 15 °C. Two film samples were investigated ($x = 0.27$ and 0.36). These films (with thicknesses about 300 nm) were prepared under nearly the same conditions. The resistance of the films was measured using a standard four-probe technique. An applied magnetic field (up to 20 kOe) was perpendicular to the film plane and to the direction of current. The results obtained were nearly the same for both films and will be illustrated by the data from the $x = 0.36$ sample. The transport properties of this film

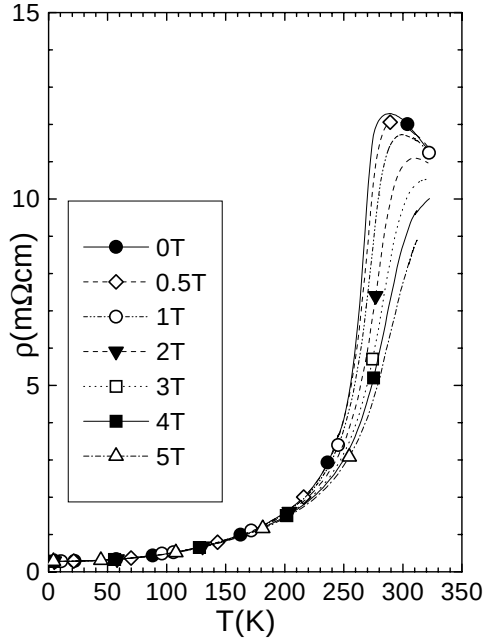

Fig. 1. Temperature dependence of the resistivity of a non-irradiated $La_{0.64}Ca_{0.36}MnO_3$ film on a $LaAlO_3$ substrate for different magnitudes of applied magnetic field.

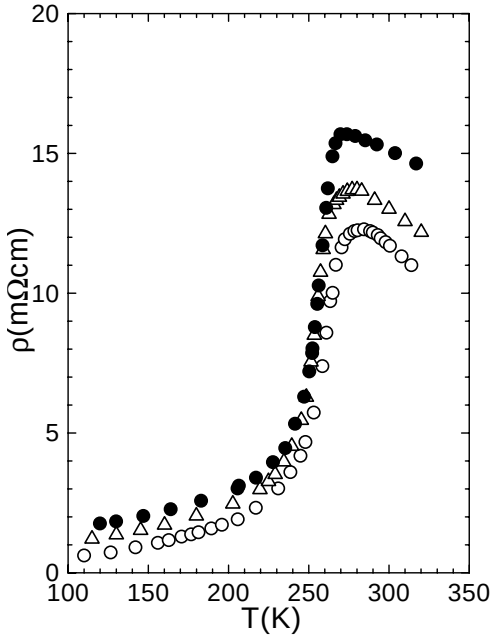

Fig. 2. Temperature dependence of the resistivity of a $La_{0.64}Ca_{0.36}MnO_3$ film on a $LaAlO_3$ substrate for different degrees of radiation damage: (○) initial state, (△) after irradiation with 6 MeV electrons at a fluence $\Phi \approx 9 \times 10^{16}$ cm^{-2}, (●) after irradiation at a total fluence $\Phi \approx 2 \times 10^{17}$ cm^{-2}.

in its initial state (before irradiation) correspond to the usual behavior of CMR films (Figs. 1 and 2). Namely, the temperature dependence of resistance $R(T)$ has a maximum (peak) at $T_p \approx 280$ K (the maximum is rather smeared). Below T_p (which for these manganite samples is always in the vicinity of the Curie point T_c) the temperature behavior of the resistance is metallic in character. The resistance R_p at T_p is about 1315 Ω (this corresponds to the resistivity $\rho = 1.24 \times 10^{-2}$ Ω cm); whereas, already at $T = 200$ K the resistance R_{200} is much less (178 Ω), and at $T = 120$ K the resistance has decreased to $R_{120} \approx 66$ Ω ($\rho = 6.25 \times 10^{-4}$ Ω cm). We have taken $\delta_H = [R(0) - R(H)]/R(H)$ at a magnetic field $H = 16$ kOe as a measure of the magnetoresistance. It can be seen from Figure 3 that δ_H has its maximum value (about 66%) at a characteristic temperature $T_m \approx 265$ K (T_m is also near T_c for these manganites).

After the first irradiation with a fluence $\Phi \approx 9 \times 10^{16}$ cm^{-2} the above mentioned parameters have changed to the following values: $T_p \approx 278$ K, $R_p \approx 1480$ Ω, $T_m \approx 259$ K, $\delta_H = 65\%$, $R_{200} = 266$ Ω, $R_{120} = 130$ Ω (Figs. 2 and 3). After a second irradiation (the total fluence after two irradiations is about 2×10^{17} cm^{-2}) these parameters are: $T_p \approx 275$ K, $R_p = 1670$ Ω, $T_m \approx 261$ K, $\delta_H = 64$ %, $R_{200} = 323$ Ω, $R_{120} = 191$ Ω.

It can be seen from these results that the electron irradiation has produced a rather large effect on film resistance. The film resistance in the paramagnetic insulating state (above T_p) has increased over 25%. More striking is the change in R in the ferromagnetic state at low temperature: $R(120)$ is tripled by the electron irradiation. At the same time (taking into account the experimental errors) there is no substantial changes of the CMR characteristics:

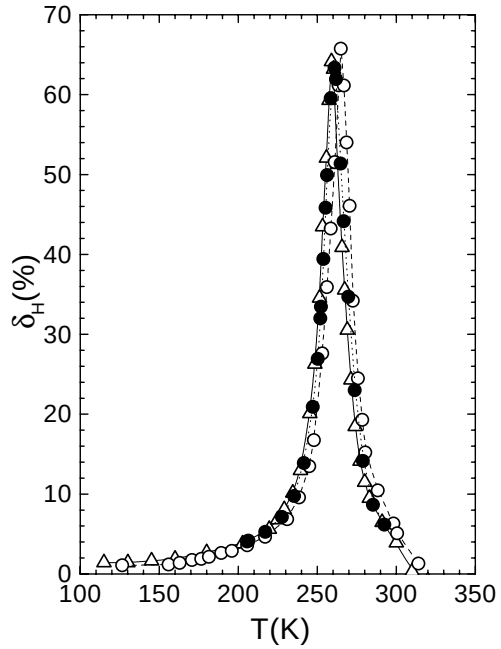

Fig. 3. Temperature dependence of the magnetoresistance δ_H for the $La_{0.64}Ca_{0.36}MnO_3$ film on a $LaAlO_3$ substrate for different degrees of radiation damage: Symbols are the same as in Figure 2.

the values of T_p, T_m (and thus T_c) decrease only about 5 K; whereas, the magnitude of the magnetoresistance δ_H remains practically unchanged.

In discussion and analysis of the results obtained it is important to determine the degree of radiation damage produced by the electron irradiation in our study.

The types of defects produced by electron irradiation are Frenkel pairs, *i.e.* isolated vacancies and interstitials. The atomic displacement cross sections by fast electrons and the corresponding values of dpa for all elements (La, Ca, Mn, and O) of the sample have been calculated taking into account the exact chemical composition of the film and using the well-known fundamental concepts of such type of relativistic calculations [23,24] and the cascade calculational procedures outlined in reference [25] together with the ratios of the Mott to the Rutherford cross section $M(x, E)$. The results of this type of calculation depend essentially on the specified value of the threshold energy $E_{\rm d}$ (an atom which receives energy $E \geq E_{\rm d}$ will be displaced certainly from its lattice site [23,24]) which was chosen to be $E_{\rm d} = 20$ eV for all ions, the typical value of $E_{\rm d}$ in common use for this type of calculation.

At the total fluence $\Phi \approx 2 \times 10^{17}$ cm^{-2} the calculations result in the following values of dpa for the chemical elements which comprise this film: 3.2×10^{-5} (La), 2.2×10^{-6} (Ca), 9.3×10^{-6} (Mn), 3.4×10^{-6} (O). The total dpa is about 4.7×10^{-5}. One should not take these values literally. As mentioned above, the output of such calculations depends essentially on the values of energy $E_{\rm d}$, which are obscure and which may be quite different for the different constituent elements. Nevertheless, we believe, based on previous studies [23–25], the calculation results should be correct at least to the order of the magnitude.

3 Discussion

The experimental results correlate, at least qualitatively, with the DE model [7–9]. In this model the ferromagnetic coupling between pairs of Mn^{3+} and Mn^{4+} ions through the oxygen ions is also responsible for the metallic properties of the manganites. The electron hopping amplitude $t_{i,j}$ from site i to site j is given by

$$t_{i,j} = b_{i,j} \cos(\theta_{i,j}/2), \tag{3.1}$$

where $b_{i,j}$ is a material-dependent constant, $\theta_{i,j}$ is the angle between the directions of two ionic spins. It can be seen from equation (3.1) that in the DE model a clear connection exists between electron transport and magnetic order, *i.e.* the electron conduction is a function of magnetic order. The angle $\theta_{i,j}$ decreases below $T_{\rm c}$ or in a magnetic field. This may be a possible reason for CMR. The disorder (for example, vacancies) must reduce the coupling between the Mn^{3+}–O–Mn^{4+} ions and, therefore, the probability of electron transfer. This must cause the increase in resistivity. At the same time the disorder should influence the ferromagnetic order (the Curie temperature $T_{\rm c}$ must go down). Therefore, the increase of disorder must induce simultaneously an increase of resistance and decrease of $T_{\rm c}$ in the DE model, that qualitatively corresponds to our results and the results of previous studies with ion-irradiated manganites [16–18].

It is usually assumed that $b_{i,j}$ in equation (3.1) is a constant for all lattice cells, which can be correct only in perfect crystals. It was taken into account in reference [18] that in disordered crystals $b_{i,j}$ is a position-dependent quantity and denotes a static disorder. The numerical simulations in reference [18] in the frame of the model for disorder-induced polaron formation [26] have shown that increasing static disorder decreases the values of $t_{i,j}$ and leads to a metal-insulator transition as observed in references [16–19].

The general approach of reference [18] (to look beyond the DE model and take into consideration additional important effects) seems to be quite fruitful. The proper consideration and interpretation of the irradiation-disorder influence is possible, however, only if the exact conduction mechanisms in the insulating and high-conducting ferromagnetic regimes of the doped manganites are known. At the moment there is still no clear enough understanding of these mechanisms. Nevertheless the experimental and theoretical achievements in this matter in the last years [3–6,10,11] enable such an attempt.

Some general observations should be noted. The magnitude of the resistance increase near and above $T_{\rm p}$ (about 25%) at first sight does not arouse great surprise, since semiconductors with a very small concentration of charge carriers are generally very sensitive to irradiation that produces displacement of atoms in the crystal. The irradiation defects quite often cause the reduction of charge carrier concentration and mobility [23,24,27]. The charge carrier concentration in doped manganites is not, however, very small. Based on the chemical doping the charge carrier concentration in $La_{1-x}Ca_xMnO_3$ ($x \approx 0.33$) should be about 0.33 holes per unit cell, a density of carriers $n \approx 6 \times 10^{21}$ cm^{-3} (for the cubic cell with lattice parameter about 0.385 nm). In Hall-effect studies of this compound it was found that in ferromagnetic state below $T_{\rm c}$ the charge-carrier density should be in the range 0.85-1.9 per unit cell [28,29]. Even higher value (2.4) was found in reference [30] for $La_{2/3}(Ca,Pb)_{1/3}MnO_3$. The reasons for such high values (which deviate much from the nominal doping level) is not clear at present [29,30]. Because of this we will assume that charge-carrier density in the ferromagnetic state corresponds roughly to 0.33 holes per unit cell ($n \approx 6 \times 10^{21}$ cm^{-3}). In the paramagnetic state not all the dopants contribute to the charge carrier density. Part of the doped holes may be localized [3,11]. Indeed, it follows from the Hall-effect measurements above $T_{\rm c}$ that in the paramagnetic insulating state the charge-carrier density is much lower, namely, in the range from 0.004 to 0.5 holes per unit cell [29–32]. We can rather safely assume that charge-carrier density above $T_{\rm c}$ decreases by at least a factor of five. This corresponds approximately to the value $n \simeq 10^{21}$ cm^{-3} which can be used for numerical evaluations. In the case of a semiconductor with activated conductivity due to a band gap or mobility edge this value appears to be too high to understand how the 10^{-5} dpa can produce this rather appreciable (about 25%) resistivity increase. Indeed, it is easy to see that even if each of the displaced ions produces a trap for the mobile charge carrier, the traps can lead to localization of only about 4×10^{18} carrier/cm^3 which is much less than estimated carrier density. Therefore, the explanation based

on the reduction in charge carrier density, which is quite usual for semiconductors [23,24,27], cannot explain the observed irradiation induced resistance increase for these manganites.

It is even more difficult to explain how such a low dpa can induce the observed threefold increase in the resistivity in the metallic ferromagnetic state at low temperature (Fig. 2). It is known [23,24,27], that 1% of displaced atoms (that is 0.01 dpa) in the noble metals like Au, Ag or Cu result in a change of resistivity of about 1 $\mu\Omega$cm. Such small changes practically could not be experimentally distinguished for these rather high-resistance manganite films. It follows that additional assumptions which take into account the peculiarities of the insulating and metallic states and the nature of the charge carriers in doped manganites are needed to explain the experimental results. For the insulating state of the doped manganites it is essential to take into account the polaronic nature of charge carriers in them (see Refs. [5,10–12,33–37] and references therein). The introduction to polaron physics and the main references can be found, for example, in reference [38]. It is rather commonly assumed that the conductivity of doped manganites above T_c is determined by small polarons [35–37]. The exact nature of these small polarons is now the object of intensive theoretical and experimental studies. The different kinds of lattice or magnetic polarons are considered. It is widely accepted that at decreasing temperature in the region of T_c the crossover from localized small polarons to itinerant large polarons takes place [39]. This point of view has found experimental support [35,40].

According to the definition [38], a lattice polaron is the unit consisting of the "self-trapped" (localized) charge carrier, together with its induced lattice deformation. The polaron is called small when the spatial extent of the wave function of the trapped charge carrier is comparable with the separation of next-neighbor ions. The polaron radius r_p for small polarons in doped manganites is estimated to be about 0.5 nm [37]. Small polarons have a large effective mass (10–100 larger than mass of free electron) and can move by tunneling or thermally activated hopping. The mobility of the small polaron is very low because the charge carrier movement includes the displacements of atoms surrounding it.

For any conductor the conductivity σ is given by the general relation $\sigma = ne\mu$, where n is density of carriers and μ is mobility. In contrast to band semiconductors in which n can depend on temperature in a thermally activated way, the density of carriers is assumed to be constant with temperature for polaronic conductors. At fairly high temperatures $T > \theta_D/2$ (where θ_D is the Debye temperature) in the adiabatic limit [38] (which is assumed to be true for the doped manganites [37,41]) it is the small polaron mobility that is activated and the resistivity $\rho = 1/\sigma$ is given by

$$\rho = \frac{2kT}{3ne^2a_h^2\omega_0}\exp(E_a/kT), \qquad (3.2)$$

where $E_a = E_b/2 - J$ is the activation energy, with E_b the polaron binding energy and J the overlap integral; a_h is the hopping distance, and ω_0 is the optical-phonon frequency.

Equation (3.2) is true in the dilute, noninteracting limit, when the density of carriers is far less than the density of equivalent hopping sites [38,41]. It may be assumed as in reference [37], that in doped manganites all the carriers form polarons. In this case with the above-estimated value of charge carrier density in the insulating paramagnetic state ($n \simeq 10^{21}$ cm^{-3}) the mean distance l_{ch} between the trapped charge carriers is ≈ 1.0 nm. Since it is assumed [38] in the general case that the hopping distance a_h is equal to a lattice constant, the noninteracting limit is quite justified for these doped manganites. For the value of dpa in this study (about 5×10^{-5}) the mean distance l_d between the damage lattice sites is about 6 nm. In reference [18] a much larger dpa (about 0.01) was produced by ion irradiation. This resulted in a tenfold increase in the resistivity in the insulating state, as compared to the approximately 25% increase shown in Figure 2 for electron irradiation. In that experiment the length l_d would be approximately 1.0 nm.

The effect of radiation damage in the insulating state of doped manganites can be understood, at least qualitatively, by taking into account the small-polaronic nature of charge carriers. Two main sources of radiation influence on small polaron conduction in doped manganites can be seen. First, according to reference [26], for the crystals with not too strong an electron-lattice interaction it is quite possible that some appreciable number of carriers would be quasifree rather than small polarons. This should be true for the doped manganites since many experimental and theoretical studies indicate [36,40,42–44] the coexistence of localized and itinerant carriers in a rather wide temperature range near T_c. In this case the disorder can convert some of the available quasifree states to small-polaron states [26]. That is, disorder reduces the strength of the electron-lattice coupling needed to stabilize the global small-polaron formation. Defects and impurities serve as centers for electron localization and small-polaron formation. This explanation is supported by the numerical simulations in reference [18]. This mechanism of the disorder-induced conductivity decrease may be dominant near T_c.

In ion-irradiation experiments [16–19] much larger dpa values (up to 0.01 and more) have been produced which have resulted in an increase in resistance in the insulating paramagnetic state by one (and sometimes two) order of magnitude. This effect is accompanied by an increase in the activation energy E_a (see Eq. (3.2)) and a decrease in peak temperature T_p. In this case, especially at temperatures rather far above T_c, it is not possible to explain the resistance increase only by the transformation of available quasi-free carriers to small polarons. These results demonstrate that the disorder influences directly the charge-carrier hopping and leads to a decrease in the charge-transfer probability. There appear to be no specific theoretical treatments of this problem for small-polaron

hopping. It is known that at high temperatures polaron jumps occur when electron energies associated with the initial and final sites (these energies are determined by a configuration of lattice atoms) are equal [38]. Maybe disorder affects these so called coincidence events in such way that it leads to a decrease in transfer probability. It should be taken into account also the possible influence of Anderson localization [3,4]. It is evident that more experimental and theoretical efforts are needed to clarify this problem.

The foregoing discussion indicates that an adequate consideration of radiation-damage effects on conductivity is possible only in the frame of a rather strictly determined conduction mechanism and charge-carrier nature. Unfortunately, no determination has been made for the ferromagnetic high-conducting state of doped manganites well below T_c. At least one assumption for this state is, however, clear: the charge carriers at low temperatures can be considered to be quasifree. It has been argued [10,33, 35,40] that the charge carriers in this state are itinerant large polarons. The polaron of this type [38] moves without thermal activation and behaves like a heavy particle (with mass in 2–4 times larger than mass of free electron). Another possibility is that the doped manganites below T_c are just degenerate semiconductors [3]. In any case the doped manganites in the ferromagnetic state with a minimal resistivity of about 100 $\mu\Omega$ cm should be considered as some kind of "bad" metal, like heavily doped semiconductors or amorphous metals. For such conductors it is quite difficult (and sometimes of no use) to estimate a value of the electron mean-free path l and consider the decrease of l under influence of irradiation-induced disorder. Indeed, for a Fermi velocity $v_F = 7.6 \times 10^5$ m/s (as was calculated in Ref. [45] for $La_{0.67}Ca_{0.33}MnO_3$) the use of the quasifree-electron relation $1/\rho = ne^2\tau/m$ with n about 1.0 hole per unit cell and m given by the mass of a free electron, gives $l = v_F\tau \approx 0.25$ nm. With an effective mass $m^* = 4m$, $l \approx 1$ nm. The films in this experiment are not single-crystal, but they do consist of rather large grains with a size near 0.5 μm. Therefore, the "intrinsic" value of l within the grains determined in this model should be larger. It is inconceiveable, however, that such considerations with a mean distance l_d between the damage sites of about 6 nm could explain the threefold increase in the resistivity of such a rather "bad" metal with an electron mean-free path on the order of 1 nm.

The unusual magnetic behavior of the doped manganites suggests a possible phenomenological explanation of the large effect of small radiation damage on the resistance in the ferromagnetic metallic regime. Irradiation not only leads to lattice disorder that can lead to elastic electron scattering as in normal non-ferromagnetic metals, but it also perturbs the long-range ferromagnetic order. In the manganites the conductivity increases with the enhancement of ferromagnetic order. Indeed, that is the source of the huge resistivity decrease at the paramagnetic-ferromagnetic transition and the CMR. Below T_c an unusual correlation between resistivity and magnetization $M(T,H)$ has been reported [35,46]. For example, in reference [35] the following experimental relation between ρ and $M(T,H)$ for the $La_{0.7}Ca_{0.3}MnO_3$ films was found

$$\rho(T,H) = \rho_m \exp\{-M(T,H)/M_0\}, \tag{3.3}$$

where ρ_m and M_0 are sample-dependent parameters. At present there is no clear theoretical understanding of this correlation between ρ and M. It is generally accepted that the increase in M should lead to delocalization of the holes and to the increase in hole mobility. In any case, however, it is clear that doped manganites are not conventional ferromagnetic metals even well below T_c, and that electronic transport in them is influenced to a high degree by magnetic order [35].

A reasonable hypothesis is that the dominant effect of irradiation on the resistivity of the doped manganites at low temperature in the ferromagnetic phase comes primarily from the disruption of long range magnetic order, perhaps through the magnetoelastic coupling that produces magnetostriction. Indirect evidence for this is provided by the observation that ion irradiation induces a considerable decrease in the saturation magnetization value M_s [18,19]. For example, in reference [19] for an ion irradiation dose which has resulted in the nearly same dpa ($\simeq 10^{-5}$) as in the present study, the saturation magnetization decreased by about 30%. Further indirect evidence of the influence of disorder effects on M_s is provided by the three-fold decrease in M_s with only a small shift in T_c that was associated with a decrease in grain size from 110 to 20 nm in bulk samples [47]. Unfortunately, the additional experimental facilities needed to test this hypothesis were not available for this experiment, but its discussion may lead to future tests of the hypothesis and generate new interest in irradiation damage studies as a way to probe the fundamental nature of conduction in these exotic materials.

In conclusion, the high-energy electron irradiation effect on the transport properties of $La_{1-x}Ca_xMnO_3$ films ($x \approx 1/3$) has been investigated. Comparatively small electron fluences used in this study do not have any substantial influence on the Curie temperature T_c or the magnitude of the magnetoresistance. At the same time these fluences result in an appreciable increase in film resistivity in both the insulating paramagnetic state and especially in the highly conductive ferromagnetic state. The relative resistivity increase in the metallic ferromagnetic state (below T_c) was found to be much (an order of magnitude) greater than that in the insulating paramagnetic state. This behavior is quite different from that associated with non-magnetic metals and semiconductors and can be understood in the high-temperature regime qualitatively by taking into account the polaronic nature of manganite's conductivity above and near T_c. A possible explanation for the low temperature behavior has been suggested, but it must be tested with magnetization measurements that were not available to the present experiments.

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39. In our discussion we will assume that small or large polarons, as well as lattice or magnetic polarons are charge carriers according to the definitions in reference [38]. At the present time in some scientific papers the term "large polaron" is sometimes used as a name for ferromagnetic droplets or clusters resulting from phase-separation or inhomogeneity effects in the doped manganites.
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