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Off-stoichiometry mechanism of the isotope effect in manganites

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A theory of the $^{16}O \rightarrow {}^{18}O$ isotope effect in the manganites is developed. It is based on the facts that an excess in the oxygen content is a thermodynamic necessity, and that it is isotope-dependent. As the excess oxygen acts as an acceptor, the charge-carrier density is isotope-dependent. On the other hand, the excess oxygen creates an internal pressure in the crystal which is also isotope-dependent. Using a realistic model for the manganites and accounting for the phonon contribution, one obtains excellent agreement with experiment and predicts the inversion of the isotope effect at elevated temperatures. The former fact makes it possible to discard the assumption that the electron-phonon coupling in the manganites is anomalously strong.

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I. INTRODUCTION

As is well known, the isotope effect can give very valuable information about the physical processes in the crystals. For this reason a very active investigation of this effect in the colossal magnetoresistance (CMR) materials was carried out recently. Early investigations of the isotope effect in the manganites[1] show that the isotope effect is large (the authors of Ref. 1 called it giant). It was discovered in Ref. 1 that replacement of ^{16}O by ^{18}O lowers the Curie point of the $La_{1-x}Ca_xMnO_3$ with x about 0.2 by 10%. Later still more impressive manifestations of the isotope effects in the manganites were found (see Ref. 2).

Based on the analogy with the standard superconductors, it was assumed in Ref. 1 that the giant isotope effect is evidence for an anomalously strong electron-phonon coupling in the manganites. But this explanation seems inadequate, as there are no special reasons to expect a very strong electron-phonon coupling in the manganites. The coupling with the optical phonons should be rather moderate, as the oxides are only partially polar crystals with a considerable weight of covalent binding. As for the coupling with the Jahn-Teller (JT) phonons which exist in the manganites, its strength has not been measured directly. If it were very strong, the doped manganites would be insulating at $T=0$ (for more detail see Sec. III). To avoid any misunderstanding, certainly the electron-phonon coupling will cause the isotope effect in the manganites, but the effect should be normal in its magnitude.

For this reason another explanation of the large isotope effect is needed. Such an explanation was proposed by the present author.[2] It is based on the fact that all the oxides display the oxygen off-stoichiometry. This off-stoichiometry is determined by the thermodynamical equilibrium conditions between a sample and the surrounding oxygen atmosphere at a temperature which depends on the way the sample cooled. Meanwhile, this off-stoichiometry influences the charge-carrier density in the sample, as the excess oxygen functions as an acceptor. In addition, it creates an internal stress in a sample, and the manganite properties are very sensitive to the stress.

But the off-stoichiometry is isotope dependent. For this reason the charge-carrier density is also isotope-dependent. Since the charge carriers realize the indirect exchange, change in their density shifts the Curie point, making it isotope dependent. In addition, an internal excess oxygen pressure is also isotope-dependent, which also leads to the isotope dependence of the electric and magnetic properties of a crystal. The excess oxygen mechanism does not depend on the electron-phonon coupling, and hence a large isotope effect does not evidence a giant electron-phonon coupling proposed in Ref. 1.

Independently of Ref. 2, an experimental investigation[3] showed that the large isotope effect in $La_{1-x}Ca_xMnO_3$ with x about 0.2 is related to the excess oxygen. Despite this fact, the authors of Ref. 1 tried to refute the theory[2] in their subsequent publication.[4] But this work is unconvincing: Since the authors did not determine the excess oxygen content of the samples, they cannot directly prove or disprove its isotope dependence. Rather, their argument is based on the similarity in behavior upon isotope replacement and under pressure, which they consider proof of the strong electron-phonon coupling. But it is unclear why they consider this similarity a manifestation of the isotope dependence of the dynamic properties of the lattice. It seems more natural to assume that the pressure mainly influences static properties. Moreover, this similarity can be explained using the ideas in the paper[2] that they criticize: The excess oxygen produces an *internal* pressure, which should cause effects of the same type as the *external* pressure.

Experimentally, the problem of the giant isotope effect was solved recently in Ref. 5, where an accurate determination of the excess oxygen content was carried out. Therein it was proved that the isotope dependence of the excess oxygen is determined by the way in which the samples are prepared. If one prepares the samples by high-temperature synthesis and then quenches them to the room temperature, then there is no isotope difference in the oxygen content, and the isotope dependence of the the Curie point is relatively weak. This result is easy to understand physically: The thermodynamic equilibrium is established at very high temperatures when the system is close to classical, and hence the isotope effect is very small in it.

But if the samples are cooled very slowly, as in Ref. 1, then the isotope difference in the oxygen content is essential. This is a consequence of the fact that the thermodynamic equilibrium is established at moderate temperatures when

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quantum effects are important.

The same Curie point shift as in Ref. 1 was found in Ref. 5. It is given by the sum of the electron-phonon and oxygen off-stoichiometry contributions, which are quite comparable. Hence only about half of the total Curie point shift can be related to the electron-phonon coupling, and there is no need to assume that it is anomalously strong.

The initial theoretical paper[2] was semiquantitative. First, a simplified model of an oxygen-rich manganite crystal was used. Second, only temperatures sufficiently low were considered when the phonon contribution to the free energy is inessential (do not confuse this contribution with the effect of the electron-phonon coupling). Meanwhile, just this contribution ensures the classical behavior of the system at high temperatures. It was found in Ref. 2 that at moderate temperatures the quantity of the excess light oxygen exceeds that of the heavy oxygen by 16%. The isotope difference in the oxygen content found experimentally in Ref. 5 is in the range between 20% and 50%. Such an agreement between theory and experiment is rather satisfactory, keeping in mind that a simplified model for a manganite crystal was used in Ref. 2.

Nevertheless, a still more correct theory of the off-stoichiometry isotope effect can be developed for the manganites. This follows from the fact that a quite similar but much more rigorous theory was developed for the Pd:H(D) system,[6] in which case the phonon contribution is taken into account. Its calculation is possible since the phonon spectra for both Pd:H and Pd:D are well known from experimental studies.[7] The theory[6] agrees with the experimental data with an accuracy of about 2% over a very wide temperature range from 170 K to 1450 K, with no fitting parameters used. So far, to construct a curve reproducing experimental data, up to nine fitting parameters were used.[7]

In the present paper a more adequate model for the manganites is used. First, it takes into account the fact that the excess oxygen atoms are not interstitial but rather enter the oxygen cage. The excess oxygen leads to the appearance of La and Mn vacancies in the crystal, in equal numbers.[8] Second, the phonon contribution to the crystal free energy is taken into account. This model leads to results markedly different from those obtained in Ref. 2.

To begin with, the present model predicts a $p^{3/4}$-like dependence of the excess oxygen content on the pressure p, whereas the model[2] predicts a $p^{1/2}$-like dependence. Further, the present model makes it possible to obtain a more accurate estimate of the effect at moderate temperatures: The quantity of the light oxygen exceeds that of the heavy oxygen by about 25%. This estimate agrees considerably better with the experimental data.[5]

As for the role of the phonons, certainly, the experimental data on the phonon spectra of the manganite crystals are currently absent, and it is impossible to calculate the isotope effect at arbitrary temperatures. But, first, the present theory can stimulate the experimentalists to investigate the phonon spectra, and, second (and this is considerably more useful at the moment), some important qualitative and even quantitative conclusions can be made even without detailed knowledge of these spectra.

Accounting for the phonon contribution to the free energy carried here leads us to predict inversion of the isotope effect at high temperatures: Not the light oxygen but the heavy oxygen becomes preponderant. This occurs in the temperature range where the motion of the atoms in the crystal is classical, but its motion inside the molecules in the gas is quantum. When the latter becomes also classical, the isotope effect disappears. Hence, the isotope effect disappears not only in the classical limit $T\to\infty$ but also at an intermediate temperature passing a minimum above this temperature.

II. CALCULATION OF THE ISOTOPE EFFECT IN THE MANGANITES

The oxygen isotope effect in the manganites of the $La_{1-x}Ca_xMnO_{3+\delta}$ type consists in the replacement of ^{16}O by ^{18}O. But the excess oxygen does not exist in the form of the interstitial atoms in the manganites. It enters the regular cage in which there are vacancies of Mn and La ions. Their numbers are approximately equal. As these ions are trivalent and oxygen is divalent, appearance of three extra oxygen ions means appearance of two Mn or La vacancies. On the other hand, this means appearance of one additional cell in the crystal with two metallic ion vacancies in the crystal.

The total free energy of the crystal with the excess oxygen consists of the energy of a perfect crystal, the energy of the excess oxygen, the configurational portion F_c^{conf} of the crystal free energy with the La or Mn ion vacancies, and from the phonon free energy with the account taken of the excess oxygen. First, F_c^{conf} will be calculated. If the number of each ion species is n, then the enlarged lattice, consisting of $N_t=(N+n)$ unit cells, should contain $2n$ ions distributed over it randomly. Then

$$F_c^{\mathrm{conf}}=-T\ln C_{N+n}^{2n}, \tag{1}$$

$$C_{N+n}^{2n}=\frac{(N+n)!}{(2n)!(N-n)!}. \tag{2}$$

Respectively, the total free energy of the crystal can be represented in the form

$$F_c=F_c^0(N+n)+nW+TN\left[2u\ln\frac{2u}{1+u}+(1-u)\ln\frac{1-u}{1+u}\right]-nf_v(T), \tag{3}$$

where W is an isotope-independent component of the work function for a pair of the ions in the crystal, $u=n/N$ is the relative number of additional unit cells in the enlarged crystal,

$$F_c^0(N)=NH_c+Nf_0(T) \tag{4}$$

is the free energy of an ideal crystal containing N unit cells, H_c is the isotope-independent chemical energy of the stoichiometric crystal per unit cell, $f_0(T)$ is the phonon free energy of the stoichiometric crystal per unit cell, and f_v is its change due to appearance of a pair of La and Mn vacancies. The phonon free energies can be expressed through effective lattice frequencies ν_0,Ω_0 for the ideal lattice and through corrections to them ν_v, Ω_v due to the excess oxygen, respectively. They are determined by the relationships

$$f_0(T)=\int_0^\infty d\omega\{T\ln[1-\exp(-\omega/T)]+\omega/2\}g_0(\omega)$$

$$\equiv 15T\ln\{1-\exp[-\nu_0(T)/T]\}+15\Omega_0/2; \tag{5}$$

$$f_v(T)=\int_0^\infty d\omega\{T\ln[1-\exp(-\omega/T)]+\omega/2\}g(\omega)$$

$$\equiv 6T\ln\{1-\exp[-\nu_v(T)/T]\}+3\Omega_v . \tag{6}$$

Here $g_0(\omega)$ is the phonon density of states in the stoichiometric crystal per unit cell, and $g_v(\omega)$ is a change in the density of states due to appearance of a pair of La and Mn vacancies. In writing Eqs. (5) and (6), the fact is taken into account that the quantities $g_0(\omega)$ and $g_v(\omega)$ after their integration over the frequencies yield the number of the freedom degrees of the stoichiometric crystal and their change due to the vacancies (per unit cell):

$$\int_0^\infty d\omega\, g_0(\omega)=15, \qquad \int_0^\infty d\omega\, g_v(\omega)=6$$

(account is taken of the fact that there are five atoms per unit cell). Unlike the zero-point mean frequencies Ω_v, Ω_0, the mean frequencies ν_v, ν_0 are temperature dependent.

The free energy of the oxygen molecules in the gas surrounding the crystal is given by the expression (e.g., Ref. 9)

$$F_g(T)=-n'D^{\text{chem}}+Tn'\left(\ln\frac{n'}{n_g}-\ln\frac{\gamma}{p}-1\right)+n'f_M(T),$$

$$f_M(T)=\omega_M/2+T\ln[1-\exp(-\omega_M/T)], \tag{7}$$

$$\zeta=\frac{2S+1}{2}T^{7/2}l^2\frac{M^{5/2}}{(2\pi)^{3/2}}, \qquad n'=\frac{n_g-3n}{2},$$

where n_g is the total number of the oxygen atoms in the system ($n_g \geqslant n$), n' is the number of the molecules in the gas, $p=n'T/V$ its pressure, V is the volume of the gas phase, M and ω_M are the oxygen atom mass and the frequency of the O_2 molecule, respectively, $S=1$ being its spin. Temperature is allowed to be comparable with the oscillation frequency of the O_2 molecule.

By minimizing the total free energy of the crystal $F_c^e + F_g$ [Eqs. (3) and (7)] with respect to the number of the La or Mn vacancies n, one finds

$$u=\frac{1}{2}\left(\frac{p}{\zeta}\right)^{3/4}\exp\left(-\frac{H_c+W+3D^{\text{chem}}/2+f_0-f_v-3f_M/2}{2T}\right), \tag{8}$$

where l is interatomic distance that practically does not depend on M. One sees that the ratio of the concentrations of the excess light (l) and heavy (h) atoms is given by

$$r=\frac{u^l}{u^h}=\left(\frac{M^h}{M^l}\right)^{15/8}P(T)Q(T)R(T), \tag{9}$$

$$P(T)=\exp\left[\frac{3(\omega_M^l-\omega_M^h)/8+3(\Omega_v^l-\Omega_v^h)/2-15(\Omega_0^l-\Omega_0^h)/4}{T}\right], \tag{10}$$

$$Q(T)=\left[\frac{1-\exp(-\nu_v^l/T)}{1-\exp(-\nu_v^h/T)}\right]^3\left[\frac{1-\exp(-\nu_0^h/T)}{1-\exp(-\nu_0^l/T)}\right]^{15/2}, \tag{11}$$

$$R(T)=\left[\frac{1-\exp(-\omega_M^l/T)}{1-\exp(-\omega_M^h/T)}\right]^{3/4}. \tag{12}$$

In analyzing the results obtained, first, it should be pointed out, that unlike the results[2], the concentration of the excess oxygen is proportional not to $p^{1/2}$ but to $p^{3/4}$ here. Further, as is seen from Eq. (9), the temperature dependence of the isotope effect is determined by the phonon spectrum of the crystal and of the oxygen molecule. Of them, the frequencies of the molecular oscillations are known: ω_M^l for $^{16}O_2$ is 0.2 eV and ω_M^h for $^{18}O_2$ is 0.19 eV.[10,11] The mean lattice frequencies entering Eqs. (9)–(12) are functionals of the phonon spectra for the stoichiometric and off-stoichiometric crystals simultaneously. In principle, they could be calculated if these spectra had been known from the experimental data, but this is not the case at present. Only frequencies for a perfect $LaMnO_3$ crystal with the light oxygen isotope are known: The frequencies of five optical modes exceed 900 K, and for one of them the frequency amounts even to 1040 K (see Ref. 12). Frequencies of other modes are between those and 300 K. Due to lack of information, a complete analysis of the temperature dependence for the isotope effect cannot be carried out at present. But nevertheless some important conclusions can be made already now.

The factor $P(T)$ at $T\rightarrow 0$ should be very large or very small depending on the sign of the exponent in Eq. (10). On increase in temperature, this factor should tend to 1. In the first case as in Pd:H the isotope effect should decrease with increasing temperature monotonically. In the second case the isotope effect should be maximal at a moderate temperature, as at classically high temperatures it should disappear at all (see below). The fact that the values of some lattice frequencies presented above are of the order of the molecular O_2 frequencies points to the possibility of both cases. The same fact allows evaluation of the temperatures at which $P(T)$ is markedly different from 1. It is sufficient to make this for the molecular contribution to the exponent of $P(T)$ equal to $3(\omega_M^l-\omega_M^h)$. It amounts to 0.004 eV. Hence, the term $P(T)$ can determine the temperature dependence of the isotope effect only at temperatures amounting to a few tens of kelvins or still lower. At higher temperatures $P(T)$ can be safely set equal to 1. As at low temperatures the oxygen diffusion in the crystal does not exist, the temperature maximum of the isotope effect is unlikely to be observable even in the case when it is possible in principle.

As for the factor $Q(T)$, it is equal to 1 at temperatures well below the typical lattice frequencies ν and diminishes with increasing temperature. One can also obtain an explicit expression for this quantity in the high-temperature region $\nu < T < \omega_M$. First, it should be noted that for $T > \nu$ the quantity $Q(\infty)$ is a constant:

$$Q(\infty) = \left(\frac{\nu_v^l(\infty)}{\nu_v^h(\infty)} \right)^3 \left(\frac{\nu_0^h(\infty)}{\nu_0^l(\infty)} \right)^{15/2}. \tag{13}$$

Further, at $T \gg \omega_M$ the isotope ratio $r(\infty)$ should have its classical value of 1. It should be recalled that this statement is a consequence of the following fact. As in the classical limit the moments and coordinates commute, the partition function is a product of factors corresponding to the kinetic and potential energies. Respectively, the free energy of any system of particles is given by the sum of ''kinetic'' and ''potential'' parts. The particle mass enters only the first term, which does not depend on the states of particles. In the case considered it does not depend on the distribution of the oxygen atoms between the crystal and the surrounding atmosphere. Hence, the number of the excess oxygen atoms in the crystal does not depend on their mass. One finds from Eqs. (9) and (12) that

$$Q(\infty) = \left(\frac{M^l}{M^h} \right)^{9/4}. \tag{14}$$

As follows from the results just obtained at temperatures between several tens and several hundred kelvins the isotope effect should be close to $(M^h/M^l)^{15/8}$, i.e., the difference between the quantities of the excess light and heavy oxygen should be about 25%. This result agrees still better with the experimental results[5] obtained for slowly cooled samples than previous results[2] calculated with the use of a simplified model (about 16% according to Ref. 2, whereas according to the experiment[5] it is between 20% and 50%).

In the high-temperature limit $\nu < T$ using Eqs. (14) and (9) one finds

$$r(T) = \left(\frac{M^l}{M^h} \right)^{3/8} \left[\frac{1 - \exp(-\omega_M^l/T)}{1 - \exp(-\omega_M^h/T)} \right]^{3/4}. \tag{15}$$

As follows from Eq. (15), at $\omega_M \gg T > \nu$ a reversion of the isotope effect takes place: Instead of the preponderant light oxygen, the heavy oxygen becomes preponderant. But the maximum value of the reversed effect is only 4.3%.

In order to elucidate the actual temperature range in which the equilibrium between a sample and the atmosphere is established, it is advisable to begin the treatment of the problem with an analysis of the experimental procedure of the isotope replacement in the manganites.[1] It is carried out about 1250 K during 48 h when almost all the oxygen sites become occupied by the corresponding isotope. Then the isotope-replaced samples are cooled very slowly in the atmosphere of the corresponding isotope with a rate of 30 K/h, so that the room temperature is achieved in more than 30 h. The concentration of the excess oxygen $3n$ must change on cooling, following the temperature of the environment. But the possibility to find exact correspondence is determined by the oxygen diffusion at this temperature, which is necessary for the oxygen exchange between the sample and surrounding atmosphere. For this reason, in reality this concentration corresponds to the equilibrium at a certain temperature, intermediate between 1250 K and 300 K when the diffusion becomes frozen.

Though in the absence of accurate data on the oxygen diffusion it is impossible to determine the freezing temperature for the excess oxygen accurately, one can use data for the oxygen diffusion in some perovskites as a reference point. The oxygen diffusion in some perovskites, e.g., in La_2CuO_4 is possible even at 230–250 K.[13] Hence, one may expect that the final off-stoichiometry reached at a slow sample cooling will correspond to 300–600 K. Such a freezing temperature is lower or comparable with their typical phonon frequencies, i.e., it is far below the classical limit when the isotope effect should disappear.

A more accurate approach should take into account a nonuniform distribution of the excess oxygen over the sample. It is worth noting that establishing the equilibrium oxygen density in the isotope-replaced sample via the diffusion can be essentially more rapid than replacing the light isotope by the heavy one as the latter process includes the replacement reaction in addition to the diffusion. The diffusion can depend essentially on the content of the acceptor impurity, so that for some compositions it can be more rapid than that for the other.

III. DOES A LARGE ISOTOPE EFFECT IN THE MANGANITES EVIDENCE AN ANOMALOUSLY STRONG ELECTRON-PHONON COUPLING?

Here the relationship between the different mechanisms of the isotope effect and the electron-phonon coupling in the manganites will be discussed. The authors of Ref. 1 tried to refute the excess oxygen mechanism,[5] and for this aim the investigation[4] was carried out, in which they claim success. On the other hand, the experimental investigations[3,5] indicate convincingly that the excess oxygen theory[2] is correct, not only qualitatively but even quantitatively. I suggest here that the paper[4] is unconvincing from the experimental point of view and incorrect from the theoretical point of view.

If the authors of Ref. 4 intend to refute the role of the excess oxygen in the giant isotope effect, first they should determine the excess oxygen content of their samples with high accuracy to compare them for two oxygen isotopes. No direct determination of the oxygen content was carried out in Ref. 4, nor even crude estimates obtained. Only indirect qualitative evidence and comparison to the results of other authors were presented to characterize the oxygen stoichiometry of the samples. But it is necessary to determine the oxygen content in the samples investigated in Ref. 4, as it depends on the manner in which the samples were prepared.[5] The fact alone that the excess oxygen content was not determined in Ref. 4 prohibits one to consider the results of Ref. 4 as a refutation of the excess oxygen mechanism.[2] Unlike Ref. 4, in Ref. 5 a very accurate determination of the oxygen content was carried out that made it possible to verify the theory.[2] Also in Ref. 4, some important quantities (e.g., pressure) are given only approximately.

The only argument in favor of the electron-phonon isotope mechanism presented in Ref. 4 is the proportionality of the isotope exponent to the pressure-effect coefficient established there. But this fact is not proof for the phonon origin of the isotope effect. Even if pressure influences the electronic properties through the lattice, this does not confirm the electron-phonon mechanism, since pressure changes not only dynamic properties but also static properties of the lattice. The contraction of the lattice under pressure can change the state of the hole system. One of the mechanisms for this is as follows: As is well known, due to the randomness in the acceptor positions, a portion of the holes is delocalized and the rest localized in the band tail. The pressure can change these portions. There also could be other non-electron-phonon mechanisms of the pressure influence on the properties of crystals.

As for the similarity between the isotope and pressure effects, one of its possible reasons can be the fact pointed out in Ref. 2: A difference in the excess oxygen contents for two isotopes produces a difference in the oxygen chemical pressures. The chemical pressure should cause effects that resemble those caused by ambient pressure. But, apparently, the authors of Ref. 4 did not recognize the corresponding statement in the theory.[2]

I conclude that the results in Ref. 4 are sufficient to confirm the existence of the isotope effect in the manganites but are insufficient to elucidate its mechanism. Meanwhile, it is established in Ref. 5 that both the electron-phonon interaction and excess-oxygen contribute to the isotope effect. If one subtracts the excess oxygen contribution from the total isotope effect one obtains the electron-phonon contribution, which has quite a normal magnitude and does not necessitate the assumption of a giant electron-phonon coupling.

This result[5] is of basic importance in establishing the mechanism of the colossal magnetoresistance (CMR) in the manganites. It would be very interesting to investigate the isotope effect in other CMR oxides, e.g., in doped EuO's in which the resistivity peak in the vicinity of the Curie point is many orders of magnitude higher than that in the manganites.

The basic problem of the physics of the manganites is an explanation of their specific features (the resistivity peak close to the Curie point and the CMR related to that peak). The authors of Refs. 1 and 4 insist on the existence of a giant electron-phonon coupling, relating it to the Jahn-Teller (JT) effect, and claim that the JT effect is responsible for the specific properties of the manganites. This idea contradicts the fact that the same features (the resistivity peak and CMR) are seen in all the numerous degenerate ferromagnetic semiconductors. But, except for the manganites, they are all non-JT systems. Hence it seems the JT effect is not responsible for the resistivity peak and CMR. On the other hand, absence of direct connections between CMR and a giant isotope effect follows directly from the fact that the latter is absent from Sr-doped manganites (see Ref. 1) though CMR in them is comparable with that of the Ca-doped samples.

Zhao *et al.* object to Ref. 2 in saying that there are different mechanisms of the resistivity peak in different materials, and the mechanism in the JT manganites is quite different than that in non-JT ferromagnetic semiconductors. But their statement does not explain why physical properties common to the JT and non-JT ferromagnetic semiconductors lead to a resistivity peak in the non-JT ones yet fail to produce such a peak in the JT ones, so that another mechanism is needed for the latter.

In fact, the moderately doped manganites are nothing other than degenerate ferromagnetic semiconductors. This explains not the similarity of the electric and magnetic properties of the manganites and other ferromagnetic semiconductors but also the well-known giant optical absorption shift, which is the most characteristic feature of the ferromagnetic semiconductors[14] and was recently observed in the manganites.[15] The necessary conditions for the resistivity peak are the ferromagnetic ordering and presence of the ionized donors (acceptors).[13,14] These conditions are certainly met in the manganites, and this is sufficient for the appearance of the peak in them.

Further, if the resistivity peak in the manganites were considerably higher than in other ferromagnetic semiconductors, it would be necessary to search for an additional mechanism for the formation of the resistivity peak, and one might think about the JT effect as such a mechanism. But the real situation is quite opposite: The height of the peak in the manganites is a few or even many orders less than in other ferromagnetic semiconductors. This height in the JT manganites is about 2–3 orders of magnitude, whereas in non-JT EuS it is 5 orders and in EuO 19 orders of magnitude (see Ref. 14). Thus one could sooner conclude that the JT effect should suppress the resistivity peak instead of producing it. I believe that in reality the JT effect influences the peak rather weakly.

One might suspect that the usual electron–optical-phonon coupling should be giant. But one should keep in mind that the manganites are only partially polar crystals with a considerable degree of covalent bonding. For this reason the polaronic effects should be rather weak in them, instead of the giant electron-phonon coupling expected in Refs. 1 and 4 (cf. Ref. 16).

It is easy to convince oneself that the assumption of giant electron-phonon coupling will lead to a direct contradiction of a basic property of the manganites: their metallic conductivity at $T=0$ resulting from their doping with acceptors. Giant electron-phonon coupling would cause the formation of low-mobility small polarons already at $T=0$. In perfect crystals a very narrow small-polaron energy band should exist at $T=0$, and Zhao *et al.*[17] try to explain the metallic properties of the doped manganites at $T=0$ by the existence of this band. But in real doped crystals the band becomes destroyed by the fluctuations of the electrostatic potential of the acceptor impurities. In essence, the crystal can become metallic only as a result of the Mott delocalization of the acceptor holes. But their orbital radius is too small for the Mott transition to take place. Such a small-polaron system should be insulating instead of metallic.

In an absolutely perfect JT crystal the $T=0$ width is $W=W_0\exp(-E_p/\omega)$, where W_0 is the initial hole bandwidth, E_p is the binding energy of the small-polaron energy, and ω is the JT phonon frequency.[18] An obvious strong inequality should be met: $E_p \gg \omega$. A necessary condition of the small-polaron existence is $W_0/2 < E_p$. As W_0 is of the order of 1 eV in the manganites one should take a value of about 1 eV for E_p to ensure small-polaron existence. Though such large E_p are unlikely to be realistic, let us look at the consequences. Taking a typical value for ω of about 0.01 eV, one finds that W should be about 10^{-43} eV, which is quite absurd for real systems in which impurities are unavoidable.

Meanwhile, for the relative impurity density in the range of 10–30 %, the electrostatic fluctuation energy F is of the order of $e^2/\epsilon a$, where is the static dielectric constant, a is the lattice constant and ϵ is the dielectric constant. For ϵ about 10 the amplitude of electrostatic fluctuations produced by ionized acceptors should amount to several tenths of an eV. Hence, it should exceed the $T=0$ small-polaron bandwidth by about 40 orders of magnitude. The destruction of the polaronic band and the small-polaron localization are inevitable under such conditions. Using the Mott delocalization criterion, one can prove that this remains in force even if $W_p = 0.1W$. Thus, the small-polaron existence is incompatible with the metallic properties.

Some authors claim to have proved the existence of the small polarons in the manganites experimentally, but these statements are related to the high-temperature small polarons arising above T_C. I do not want to discuss that problem as it is irrelevant to the $T=0$ small-polaron band theory discussed here. A detailed analysis of the situation with the high-temperature small polarons may be found in my review articles on the manganites.[19]

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