

## Pressure dependence of the metal-insulator transition in the charge-transfer oxides $RNiO_3$ ( $R = Pr, Nd, Nd_{0.7}La_{0.3}$ )

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We have investigated the pressure dependence (up to 20 kbar) of the metal-insulator (MI) transition displayed by the orthorhombic perovskites  $RNiO_3$  ( $R = Nd, Pr, \text{ and } Nd_{0.7}La_{0.3}$ ) by means of electrical resistance measurements. The transition temperature decreases under pressure, with a common rate of decrease of  $dT_{MI}/dP = -4.2$  K/kbar, in spite of differences in  $T_{MI}$  (100–200 K). On the basis of the structural effects associated with the application of pressure in these orthorhombic perovskites, we conclude that the metallic phase is stabilized by pressure because the bandwidth increases and hence the charge-transfer gap is reduced. This decrease with pressure of the charge-transfer gap in the  $RNiO_3$  perovskites is in contrast to the dependence predicted and observed in the layered cuprates where the charge-transfer energy dominates the bandwidth effects. In addition, our experiments show that the first-order phase transformation occurring at  $T_{MI}$  is inhibited by pressure, and hence a larger proportion of metallic phase occurs, which leads to an apparent reentrant metallic behavior at low temperature.

There exists considerable evidence from spectroscopic investigations for a charge-transfer nature of the gap in the insulating layered cuprates.<sup>1,2</sup> When suitable doping is achieved, a metallic state is formed with new midgap states.<sup>3</sup> It is clear then that there is a general rearrangement of the electronic states associated with the metallic electrons. Hence, it appears difficult to consider this transition as prototypical of charge-transfer insulators because electronic, steric and chemical modifications, as well as disorder, are introduced simultaneously.

In the past, extensive analysis of the MI transition in Mott-Hubbard oxides was performed in prototypical systems, such as  $V_2O_3$  or  $Ti_2O_3$ , where the transition can also be induced by varying solely the temperature or the pressure.<sup>4</sup> The recent discovery of a metal-insulator transition in the charge-transfer oxides  $RNiO_3$  ( $R = \text{rare earth}$ ) is particularly rewarding.<sup>5</sup> After a systematic study of the dependence of  $T_{MI}$  on the rare earth ionic radius, Torrance *et al.* concluded that, upon lowering the temperature, the bandwidth increases and induces a closing of the charge-transfer gap.<sup>6</sup> Furthermore, the transition has a weak first-order character with very small structural modifications which are associated only with the differences of atomic radius in the metallic and

insulating phases.<sup>6,7</sup> In addition, muon spin rotation<sup>7</sup> and neutron diffraction studies have shown that long-range magnetic order appears in the insulating state of  $PrNiO_3$  and  $NdNiO_3$ .<sup>8</sup>

The charge-transfer character of the gap in  $RNiO_3$  perovskites was inferred from simple calculations<sup>9</sup> which are based on the ionic model proposed by Torrance and Metzger,<sup>10</sup> where the charge-transfer energy  $\Delta$  only depends on atomic parameters (i.e., the electron affinity of  $O^{2-}$  and the ionization energy of  $Ni^{3+}$ ) and on the difference of the Madelung site potentials. This simple model seems to give a consistent classification of the electrical nature of the transition metal oxides<sup>9</sup> and also seems to account for the different charge-transfer gaps observed in the insulating cuprates.<sup>11</sup>

In this work we report a study of the pressure dependence of the metal-insulator transition in  $RNiO_3$  oxides.

Referring now to the gap closure process that occurs in  $RNiO_3$  perovskites, it is important to know if the metallic state is stabilized by pressure, similar to Mott-Hubbard insulators, or if, instead, the charge-transfer gap  $E_g$  increases with pressure, as has been suggested as being a general feature of charge-transfer oxides.<sup>11</sup>

The behavior of the gap with pressure depends on a

delicate balance between different energy terms: the bandwidth  $W$  and  $\Delta$  in charge-transfer oxides or  $U$  in Mott-Hubbard insulators. In layered cuprates, for instance, it has been suggested that  $\Delta$  increases with pressure at a greater rate than does the bandwidth  $W$ , thus suggesting that the insulating phase is stabilized with pressure.<sup>11</sup> In the scope of the ionic model, the increase of  $\Delta$  with pressure is attributed to a greater Madelung site potential for a hole located on the copper than on the in-plane oxygen.

We will show in this paper that the metallic state is stabilized under high pressure in  $R\text{NiO}_3$  perovskites because the bandwidth increase dominates. We may therefore conclude that there is no general rule governing the pressure dependence of the gap in charge-transfer oxides.

The synthesis of  $R\text{NiO}_3$  ( $R = \text{Pr}, \text{Nd}, \text{Nd}_{0.7}\text{La}_{0.3}$ ) polycrystalline samples was performed under an oxygen pressure of 200 bar in order to preserve the correct oxygen stoichiometry. The samples have been extensively characterized by x-ray diffraction, differential scanning calorimetry (DSC) measurements, neutron diffraction, and electrical and magnetic investigations.<sup>5–8,12</sup>

The electrical resistivity as a function of temperature under pressure was measured in a beryllium-copper self-clamping device similar to the one described in Ref. 13. The pressure transmitting fluid was a 1:1 mixture of isoamyl alcohol and *n*-pentane. This mixture is known to be a good quasihydrostatic pressure transmitting medium.<sup>14</sup> Measurements of the electrical resistivity were made by means of a four lead ac technique at a frequency of 16 Hz. All the measurements were performed with heating rates of about 0.2°C/min, in order to minimize the temperature difference between the thermometer and the sample.

The general picture of the electrical resistance of  $R\text{NiO}_3$  perovskites displaying metal-insulator transitions has already been reported by several authors.<sup>5,6,12</sup> Essentially, a high-temperature metalliclike behavior is observed with a linear decrease of the resistance  $R$  with decreasing temperature, and a sudden increase of  $R$  at  $T_{\text{MI}}$ . We note that following a cooling procedure, the transition is much smoother because of hysteresis in the degree of phase transformation.

The sharp change in electrical resistivity at  $T_{\text{MI}}$  makes it possible to follow the dependence of  $T_{\text{MI}}$  on pressure unambiguously, as displayed in Fig. 1 in the case of  $\text{NdNiO}_3$ . These measurements show that the metallic resistivity is essentially unchanged while the onset of the metal-insulator transition decreases at a rate of  $-4.2$  K/kbar. It may also be observed that the initial slope of the resistivity in the insulating phase is very similar in all the reported measurements up to 20 kbar. At low temperatures, a behavior typical of thermally activated semiconductors has been found in  $\text{PrNiO}_3$  and  $\text{NdNiO}_3$  with an activation energy for  $\text{PrNiO}_3$  of about 22 meV.<sup>12</sup>

A similar decrease of  $T_{\text{MI}}$  with pressure has been found in  $\text{PrNiO}_3$  [Fig. 2(a)]. Now, however, a progressive decrease of the apparent activation energy in the semiconducting phase is observed initially; finally, a new reentrantlike metallic behavior develops at low temperatures which becomes more prominent upon increasing the pres-

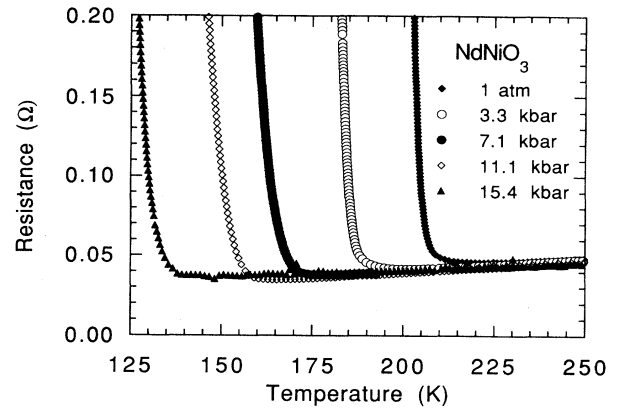


FIG. 1. Resistance of  $\text{NdNiO}_3$  as a function of temperature at five different pressures.

sure [Fig. 2(b)]. It is straightforward to note that pure metallic behavior was observed in  $\text{PrNiO}_3$  beyond a critical point ( $T_{\text{cr}}, P_{\text{cr}}$ ) with  $P_{\text{cr}} \cong 11.6$  kbar and  $T_{\text{cr}} \cong 65$  K.

A similar behavior was found in  $\text{Nd}_{0.7}\text{La}_{0.3}\text{NiO}_3$ , where at atmospheric pressure  $T_{\text{MI}} \cong 103$  K. The overall pressure dependence of  $T_{\text{MI}}$  in these three compounds is displayed in Fig. 3, where the pressure scale has been shifted in the different compounds in order to make the

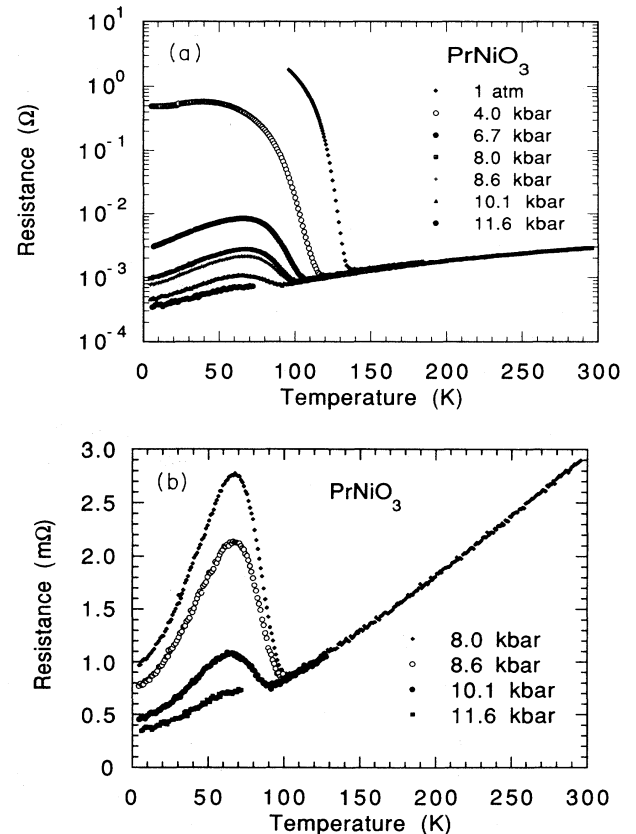


FIG. 2. (a) Semilog plot of the resistance of  $\text{PrNiO}_3$  as a function of temperature at pressures ranging from 1 atm to 11.6 kbar. (b) Detail of the resistance of  $\text{PrNiO}_3$  as a function of temperature for pressures greater than 8.0 kbar.

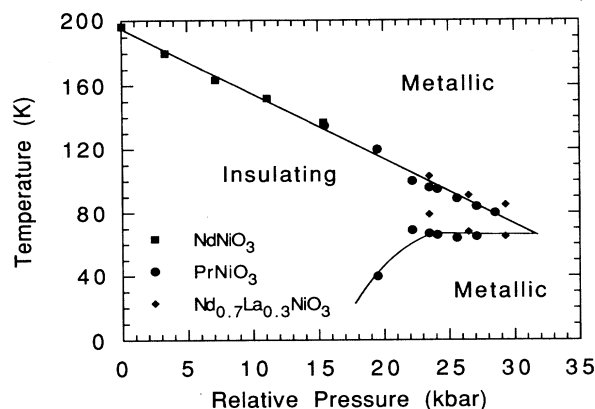


FIG. 3. Phase diagram of the  $R\text{NiO}_3$  ( $R = \text{Nd}$ ,  $\text{Pr}$ , and  $\text{Nd}_{0.7}\text{La}_{0.3}$ ) perovskites, where the pressure has been shifted by 15.5 kbar for  $\text{PrNiO}_3$  and by 24 kbar for  $\text{Nd}_{0.7}\text{La}_{0.3}\text{NiO}_3$  in order to make the common linear decrease of  $T_{\text{MI}}$  with pressure more evident. Solid lines are guides to the eye.

common characteristics of the phase diagram of all these orthorhombic perovskites more evident. This figure shows that the line  $T_{\text{MI}}$  vs  $P$  separating the metallic state from the antiferromagnetic-insulating phase has a universal character in the  $R\text{NiO}_3$  perovskites: i.e., the rate of decrease of  $T_{\text{MI}}$  with pressure is independent of the rare-earth ion. This feature seems to indicate that a common structural and electronic parameter is controlling the evolution of  $T_{\text{MI}}$  with pressure. It also suggests that a critical point signaling, the beginning of a pure metallic regime, is a characteristic common to all these oxides. In  $\text{Nd}_{0.7}\text{La}_{0.3}\text{NiO}_3$ , the insulating phase disappears at the same temperature as the  $\text{Pr}$  oxide and a critical pressure of  $P_{\text{cr}} \cong 7.5$  kbar (Fig. 3). If we assume that  $T_{\text{cr}}$  is the same in all these perovskites our phase diagram predicts that  $P_{\text{cr}} \cong 31$  kbar for  $\text{NdNiO}_3$ , which is beyond the maximum pressure attainable with our cell.

Before starting a full analysis of the main subject of the present work, i.e., the microscopic mechanisms associated with the pressure dependence of the metal-insulator transition in the  $R\text{NiO}_3$  charge-transfer oxides, we need to discuss the origin of the anomalous low-temperature behavior of the resistivity in  $\text{PrNiO}_3$  and  $\text{Nd}_{0.7}\text{La}_{0.3}\text{NiO}_3$ , i.e., the observation of reentrant metallic behavior at low temperatures.

In a recent work, Granados *et al.*<sup>12</sup> have investigated the metastability of the metallic phase below  $T_{\text{MI}}$  and the hysteretic behavior associated with the first-order character of the MI transition in  $R\text{NiO}_3$  perovskites. From transport measurements (electrical resistivity and Seebeck effect), these authors concluded that a wide temperature range exists where both phases coexist and that the percentage of phase transformation is hysteretic and time dependent.

Actually, this electronic transition bears some similarities to the martensitic phase transformations where lattice distortions occur without atomic diffusion. In these transformations there is a balance between a driving force (thermodynamic stabilization of a new phase) and the elastic accommodation of the strain energy generated by

the volume change. The local balance between these terms leads to the formation of interfaces, a phase coexistence in a certain temperature interval, and relaxation processes. Furthermore, it is well known that this thermal hysteresis may be strongly modified under pressure.

We believe this is the main source of the anomalies observed in  $\text{PrNiO}_3$  under pressure and in  $\text{Nd}_{0.7}\text{La}_{0.3}\text{NiO}_3$  at any applied pressure. If the metallic phase remains dominant at temperatures well below  $T_{\text{MI}}$ , we should first observe an increase in resistivity at  $T_{\text{MI}}$  due to the formation of some insulating phase, but finally, if the growth rate of the secondary phase (insulating phase) is slowed down at low temperatures, the character of the dominant phase should be preserved and metallic behavior reappears at low temperature. Within this context the observation of a maximum in the electrical resistance at low temperature may be understood simply in terms of a transition between two effective metallic media having different electrical resistivities. The meaning which we attribute to the critical point is that below  $T_{\text{cr}}$  the growth of the low-temperature insulating phase is essentially frozen out because of a restricted mobility of the different atomic species.

It is important to note that, while the resistivity is hysteretic below  $T_{\text{MI}}$ , the transition temperature itself is not hysteretic; i.e., it is the same whether determined upon heating or cooling.

We would now like to focus our attention on the problem of the pressure dependence of  $T_{\text{MI}}$  in the  $R\text{NiO}_3$  perovskites and its significance from the point of view of the electronic structure of these materials. A full understanding of the origin of a common linear decrease with pressure of  $T_{\text{MI}}$  in all the investigated perovskites requires careful consideration of all the steric effects existing in these orthorhombic perovskites when temperature, pressure, and rare-earth size are modified.

The crystal chemistry of orthorhombically distorted perovskites ( $Pmmm$  space group) was analyzed by O'Keeffe *et al.*,<sup>15</sup> and they showed that simple relationships may be written among the lattice parameters, the ionic radius of rare-earth and Ni cations [or the tolerance factor  $t = (d_{R-O})/\sqrt{2}(d_{Ni-O})$ ] where  $d_R$  and  $d_N$  are the rare-earth-oxygen and nickel-oxygen distances, respectively, and the tilting angle of the octahedra  $\phi$  ( $\phi = 180 - \theta$ , where  $\theta$  is the Ni-O-Ni angle).

It is a simple matter then to understand that the general phase diagram of  $R\text{NiO}_3$  perovskites proposed by Torrance *et al.*<sup>6</sup> relating the location of the metal-insulator transition with the tolerance factor  $t$  is essentially representing  $T_{\text{MI}}$  as a function of the tilting angle  $\phi$ . It has been found experimentally that the orthorhombic distortion (and hence  $\phi$ ) decreases when  $t$  (or the rare-earth ionic radius) increases. For instance, we have  $\phi = 27.4^\circ$  in  $\text{SmNiO}_3$  and  $\phi = 21.3^\circ$  in  $\text{PrNiO}_3$ .

It is clear then that the tilting angle  $\phi$  seems to play an essential role in determining when the metal-insulator transition occurs. If this transition is associated with a closing of the charge-transfer gap separating the oxygen  $2p$  valence band and the unoccupied Ni  $3d$  conduction band, we should analyze the dependence of  $E_g = \Delta - W$

on pressure and temperature.

The temperature and pressure dependences of  $\phi$  are directly related to the bond expansivity ( $\alpha$ ) and bond compressibility ( $\beta$ ), respectively, of the rare-earth and Ni ions through the simple relationships:<sup>15</sup>

$$(\partial \cos\phi / \partial T)_P \propto (\alpha_R - \alpha_N) \cos\phi, \quad (1)$$

$$(\partial \phi / \partial P)_T \propto (\beta_R - \beta_N) \cos\phi. \quad (2)$$

Clearly, the relative strength of the R-O and Ni-O bonds determines if the orthorhombicity increases or decreases with temperature and pressure. The temperature dependence of  $\phi$  in PrNiO<sub>3</sub> and NdNiO<sub>3</sub> oxides has been measured by Huang *et al.*<sup>16</sup> and Garcia-Munoz *et al.*,<sup>7</sup> and they found a slight decrease when  $T$  increases thus indicating that  $\alpha_R$  is greater than  $\alpha_N$ , in agreement with previous investigations of distorted perovskites.<sup>16</sup> From a chemical point of view we should also expect that the compressibility of the R-O bond is higher than the Ni-O bond and so Eq. (2) tells us that  $\phi$  should increase when we apply pressure. This was actually observed by Mao *et al.*<sup>17</sup> in a study of the orthorhombic perovskites (Fe,Mg)SiO<sub>3</sub>.

We should now consider the electronic consequences of all of the above mentioned steric effects. As discussed previously by Torrance *et al.*<sup>6</sup> and Sawatzky *et al.*,<sup>18</sup> a decrease of  $\phi$  has a strong effect on the degree of orbital overlapping (Ni 3d and O 2p) and hence the bandwidth increases if  $\phi$  decreases. It is straightforward to note, however, that  $d_R$  and  $d_N$  are also reduced with either temperature or increasing pressure. When  $\phi$  is small we should expect that  $W \cong W_0 \cos\phi$ , where  $W_0$  is the bandwidth in a nondistorted perovskite which will depend on  $d_N$  following a power law, typically  $W_0 \sim d_N^{-3}$ .<sup>19</sup> Therefore, taking into account that in these orthorhombic perovskites we have  $\cos\phi \sim (d_R/d_N)^x$ ,<sup>16</sup> we get

$$W \sim (d_R^x / d_N^{3+x}) \quad (3)$$

and

$$1/W (dW/dT)_P \sim \alpha_R - [(3+x)/x] \alpha_N, \quad (4)$$

$$1/W (dW/dT)_T \sim \beta_R - [(3+x)/x] \beta_N. \quad (5)$$

These equations allow us to examine which is the dominant factor in determining  $W$ . First of all, the stabilization of the metallic phase at high temperatures indicates

that the decrease of  $\phi$  when  $T$  is increased overrides the thermal expansion effects which should decrease  $W_0$ , i.e.,  $\alpha_R > [(3+x)/x] \alpha_N$  as indicated by Eq. (4). The same conclusion is reached when the dependence of  $T_{MI}$  on  $t$  (or  $d_R$ ) is analyzed. While it should be expected that a reduction of the interatomic distance should increase  $W$  and hence stabilize the metallic phase, the opposite trend is observed, i.e., the metallic phase is favored when  $d_R$  increases, thus signaling that an enhanced bond overlapping is reached through a decrease of  $\phi$  because  $d_N$  remains nearly constant.

Finally, the application of pressure leads to an increase of  $\phi$  as signaled by Eq. (2), but this does not necessarily imply that  $W$  decreases because  $W_0$  might have a stronger increase through the reduction of the Ni-O bond. Actually, the condition for an overriding effect of the bond compressibility is that  $\beta_R > [(3+x)/x] \beta_N$ , as indicated by Eq. (5). Our experimental results indicate that the metallic phase is stabilized by external pressure, so we are forced to conclude that this condition is fulfilled.

As we have already mentioned, in layered cuprates it has been suggested that this is the leading term in the pressure dependence of  $E_g$  (Ref. 11) which should increase under high pressure. Although there are no estimations of the pressure dependence of  $\Delta$  in RNiO<sub>3</sub>, the calculations reported by Torrance *et al.*<sup>9</sup> based on an ionic model<sup>10</sup> suggest that the Madelung energy driving  $\Delta$  should not be modified very much. It is then very unlikely that the decrease of  $E_g$  under pressure required by our experiments is due to changes in  $\Delta$ .

In summary, we have observed an enhanced stability of the metallic phase under pressure in RNiO<sub>3</sub> perovskites which may be explained by a decrease of the charge-transfer gap  $E_g$ . We suggest that the closing of the gap is associated with an increase of the bandwidth  $W_0$  with pressure. The main conclusion of our work is that there is no unique behavior concerning the pressure dependence of  $E_g$  in charge-transfer oxides. A careful analysis of the different energetic terms involved is necessary to reach a firm conclusion.

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