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Extraordinary pressure dependence of the metal-to-insulator transition in the charge-transfer compounds $NdNiO_3$ and $PrNiO_3$

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The pressure dependence of the metal-to-insulator transition in $NdNiO_3$ and $PrNiO_3$ has been studied up to applied hydrostatic pressures of 16 kbar. In both cases the first-order metal-to-insulator phase transition is extremely sensitive to pressure, with 15.1 kbar suppressing the transition from 196 to 103 K in $NdNiO_3$ and 14.1 kbar suppressing the transition from 130 to below 1.5 K in $PrNiO_3$. Analysis of the data within the framework of charge-transfer gap insulators leads to the prediction that the primary effect of pressure is to straighten the Ni-O-Ni bond angle, leading to a broadening of the lower, oxygen-like valence band.

Metal-to-insulator (MI) transitions have always been of great interest to solid state physicists and chemists. Systems such as VO_2 (Ref. 1), V_2O_3 (Ref. 2), and the V_NO_{2N-1} (Ref. 3) Magneli series have been studied in detail in hopes of understanding the underlying physics of their individual MI transitions, but in each case, the first-order phase transition is accompanied by a structural distortion that changes the symmetry of the low-temperature, insulating state. Members of the RNiO$_3$ series (R=rare earth), which form in the orthoferrite structure, manifest MI transitions below 500 K for R=Pr, Nd, Sm, and Eu.[4] The MI transition is not accompanied by any change in lattice symmetry, only a slight expansion of the unit cell on cooling into the insulating state. In addition, the RNiO$_3$ materials are members of a wider family of charge-transfer-gap compounds[5,6] having a p-like valence band and a d-like conduction band. The MI transition has been proposed to be due to a band crossing, which results in the closing of the charge-transfer gap, associated with the thermal broadening of the lower, oxygen-p-like band.[4] The simplicity of both the materials and the proposed mechanism responsible for the MI transition make the RNiO$_3$ family an ideal system for the study of the effects of hydrostatic pressure on charge-transfer-gap materials. In this paper we will present data on the effects of hydrostatic pressure on both $NdNiO_3$ and $PrNiO_3$ (the members of the RNiO$_3$ family with the lowest two metal-to-insulator transition temperatures, $T_{\rm MI}$'s). The data will be analyzed within the framework of charge-transfer-gap materials, which brings new insight to the pressure dependence of iron group, late transition metal oxides.

Polycrystalline specimens of Nd(Pr)NiO$_3$ were prepared by solid state reaction under high oxygen pressure.[7] Powders of Nd_2O_3 (Pr_6O_{11}) and $Ni(NO_3)_2{\cdot}6H_2O$ were thoroughly mixed, pressed into a pellet, and then dried at 600 °C for five hours. The dried pellet was then reacted at 1000 °C under an oxygen pressure of 200 bars for twenty hours. The pellet was reground, repelletized, and then the high pressure reaction was repeated. The magnetic susceptibility was measured with a Quantum Design superconducting quantum interference device (SQUID) magnetometer and electrical resistivity was measured using a standard four probe configuration and a LR-400 a.c. resistivity bridge. Cooling and warming rates during the measurement of the electrical resistivity were approximately 1 K per minute for every pressure. Since the samples were polycrystalline pellets, the absolute value of the resistivity is only reliable to within roughly 10%. Hydrostatic pressures were applied using the self-clamping cell and C_6F_{12} (Flourinert FC-75) as pressure media.[8]

Figure 1(a) shows the derivative of $T\chi(T)$ as a function of temperature for the $NdNiO_3$ sample. The form of $d[T\chi(T)]/dT$ is similar to $C_P(T)$ (Ref. 9) for antiferromagnetic transitions, and is indicative of the antiferromagnetic transition accompanying the MI transition in $NdNiO_3$. The shape and position of the $d[T\chi(T)]/dT$ curve is insensitive to the highest applied field of 4 T. The value of $T_{\rm MI}$ found by this method agrees with that found by the logarithmic derivative of the temperature-dependent resistivity[10] which uniquely defines the value of $T_{\rm MI}$, as opposed to simple inspection of the $\rho(T)$ plot. The slight difference in the $T_{\rm MI}$'s (approximately 2 K) determined by these two measurements (both taken on warming the sample) is very likely due to the hysteretic nature of the MI transition and/or differences in the warming rate between the two measurements. Figure 1(b) shows the natural log of the electrical resistivity as a function of temperature for four representative applied pressures. The hysteresis in the resistivity seen below $T_{\rm MI}$ is seen in all samples of Nd(Pr)NiO$_3$ examined. The existence of hysteresis and the qualitative shape of $\rho(T)$ indicate that the MI transition is first order. Whether the width of the hysteresis loop is intrinsic to the material, or a nuance of its polycrystalline form is not resolved. As

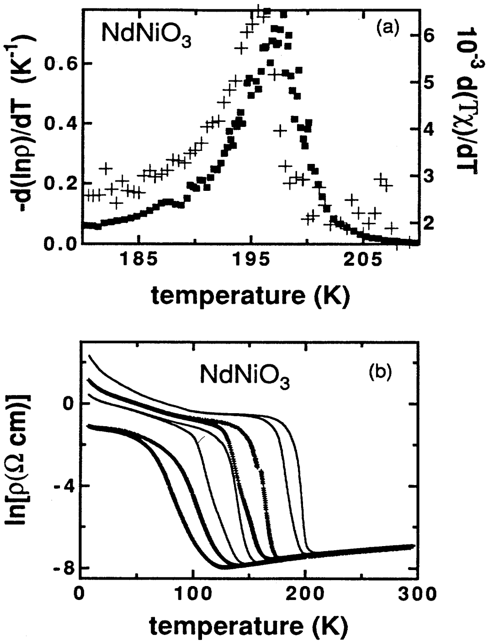

FIG. 1. (a) Derivative of χT with respect to temperature at a field of 2 T (crosses) and the logarithmic derivative of temperature-dependent resistivity (solid squares) of $NdNiO_3$. Both measurements are at ambient pressure and are warming data only. Units of the $d(T\chi)/dT$ are emu/(f.u. mole K). (b) Temperature dependence of natural log of resistivity of $NdNiO_3$ shown for applied pressures of 1 bar, 5.4 kbar, 10.6 kbar, and 15.1 kbar. Data sets for each pressure are shown alternately as solid lines and crosses. The furthest right data set (solid line) is 1 bar data and the furthest left data set (crosses) is 15.1 kbar data. For each data set the further right curve is the warming data.

pressure is increased T_{MI} is suppressed, the size of the jump in resistivity associated with T_{MI} decreases, and the width of the transition, as manifested in the width of the peak in $1/R\ dR/dT$, increases.

The pressure dependence of the electrical resistivity of $PrNiO_3$ is shown in Fig. 2(a). At ambient pressure a plot of $\ln(\rho)$ vs $1/T$ has no significant region of linearity, but the value of the semiconducting gap can be estimated to be no greater than 200 K. As with $NdNiO_3$, the application of pressure suppresses the MI transition. In the case of $PrNiO_3$, though, since the ambient pressure MI transition occurs at 130 K, 14.1 kbars is sufficient to suppress the MI transition to below 1.5 K. T_{MI} can easily be determined in the cases of 1 bar, 5.2 and 9.0 kbars applied pressures, but since there is virtually no increase in the resistivity with decreasing temperature for 10.8 kbars of applied pressure the exact value of T_{MI} is poorly defined. There is clearly a MI transition near 40 K, though, as is manifested by the break in the slope of $\rho(T)$ and the hysteresis that is associated with the MI transition. This is in contrast with the $\rho(T)$ curve for the applied pressure of 14.1 kbars. At this pressure there is no hysteresis, and the slope monotonically changes as temperature changes, both indications that the material is truly metallized. The resistivity can be fit to a $T^{1.63}$ power law between 1.5 and 150 K. It should be noted, in passing, that when the MI transition is totally suppressed, the residual resistivity ratio of the sintered $PrNiO_3$ pellet is better than 20. Figure 2(b) shows the natural log of the resistivity as a function of temperature for the same data shown in Fig. 2(a). The suppression of the jump in resistivity associated with the MI transition is much more dramatic in $PrNiO_3$; with a change of six orders of magnitude in the low-temperature resistivity between 1 bar and 14.1 kbar.

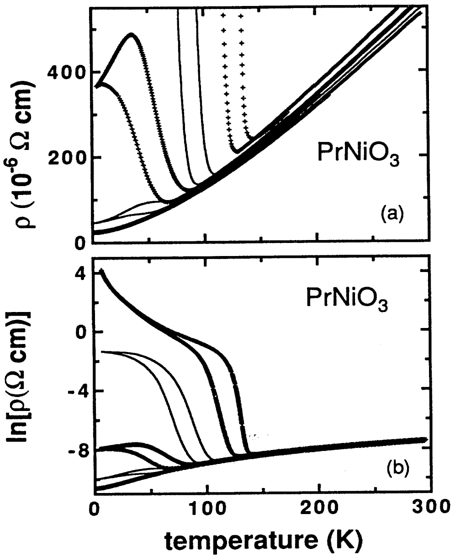

FIG. 2. (a) Temperature-dependent resistivity of $PrNiO_3$ for applied pressures of 1 bar, 5.2 kbar, 9.0 kbar, 10.8 kbar, and 14.1 kbar. Data sets for each pressure are shown alternately as solid lines and crosses. The furthest right data set (crosses) is 1 bar data and the furthest left data set (crosses) is 14.1 kbar data. For each data set the further right curve is the warming data. (Note: for the 14.1 kbar data set there is no hysteresis and therefore no difference between warming and cooling data.) (b) Temperature dependence of the natural log of the resistivity of $PrNiO_3$ at the same pressures.

Figure 3(a) plots T_{MI} as a function of pressure. The T_{MI} values used are from the warming data for each pressure. The sensitivity of T_{MI} to pressure in this system is remarkable. In $NdNiO_3$, T_{MI} is suppressed, on average, by −6.1 K/kbar over the 15.1 kbar range examined, and in $PrNiO_3$, T_{MI} is suppressed, on average, by −9.2 K/kbar over the 14.1 range examined. The only other oxide system that has a similar sensitivity of T_{MI} to pressure is V_8O_{15} which has its T_{MI} suppressed from 67 K to below 1.2 Kk with a 14 kbar applied pressure (−4.8 K/kbar).[3,11]

In Fig. 3(a) the T_{MI} of $PrNiO_3$ is also plotted with the pressure scale shifted by 11.7 kbar. This shift allows the data to overlap T_{MI}'s. It should be noted that the matching of slopes of the T_{MI} data is inherent to the data, and is not adjustable. This match of the $NdNiO_3$ and $PrNiO_3$ data suggests that there should be some unifying parameter that will allow these two materials to become part of a single phase diagram. The simple idea of chemical pres-

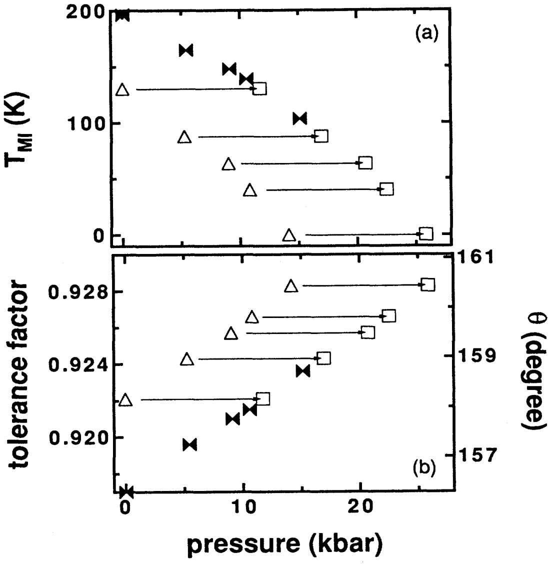

FIG. 3. (a) T_{MI} as a function of applied pressure for $NdNiO_3$ (solid symbols) and $PrNiO_3$ (open triangles). $PrNiO_3$ data also shown shifted by 11.7 kbar (open squares). (b) Tolerance factor and Ni-O-Ni angle (both defined in text) for $NdNiO_3$ (solid symbols) and $PrNiO_3$ (open triangles) as a function of applied pressure. $PrNiO_3$ data also shown shifted by 11.7 kbar (open squares).

sure is not this parameter, since the lattice parameters of $PrNiO_3$ are larger than those of $NdNiO_3$, as would be anticipated by the lanthanide contraction. Invoking chemical pressure for the shift of 11.7 kbar would give the wrong sign to the pressure shift. The most likely parameter is the tolerance factor of the underlying perovskite structure. An examination of Fig. 2 in Ref. 4 shows that there is a strong correlation between T_{MI} and tolerance factor. Using this phase diagram, the tolerance factor associated with a given T_{MI} can be determined. Figure 3(b) plots the pressure dependence of the tolerance factor as a function of pressure for $NdNiO_3$ and $PrNiO_3$, with the $PrNiO_3$ data appearing with shifted and unshifted pressure scales.

The tolerance factor is the ratio of the R-O bond length to the Ni-O bond length: $t=(d_{R\text{-O}})/[\sqrt{2}(d_{\text{Ni-O}})]$. A change in the tolerance factor can be associated with a change in either or both of these bond lengths. Another, in fact more physical, way of parametrizing the lattice mismatch of this structure is to use the Ni-O-Ni bond angle. The tolerance factors for $SmNiO_3$, $PrNiO_3$, and $LaNiO_3$ are $t=0.906$, 0.923, and 0.940, respectively, and the Ni-O-Ni angles are 152.6°, 158.7°, and 165.2°, respectively.[4] From these three points a linear relation between tolerance factor and Ni-O-Ni bond angle (θ) can be approximated by $\theta=367.6t-180.8$. The right-hand side of Fig. 3(b) shows the pressure dependence of θ. The pressure dependence of θ can be used to explain the suppression of the MI transition in exactly the same way that the temperature dependence of the ambient pressure resistivity has been explained.[4] As pressure (temperature) is increased the Ni-O-Ni angle increases, causing the oxygenlike band to broaden to such an extent that it overlaps with the higher Ni-like band. When these bands cross Nd(Pr)NiO_3 acquires a finite density of states at the Fermi surface and the MI transition occurs.

The hypothesis that the suppression of the MI transition is due to a pressure induced straightening of the Ni-O-Ni angle may, at first glance, appear unusual, but an examination of the crystal structure of the orthoferrites reveals this to be a plausible explanation. The tilting of the NiO_6 octahedra is due to a mismatch of the rare-earth size and the space between the corner-sharing octahedra: the rare earths are too small to fill this space, therefore causing the NiO_6 octahedra to tilt in order to make the space smaller. Pressure reduces the size of the space and consequently reduces the mismatch, resulting in the decrease of the NiO_6 octahedra's tilting and the straightening of the Ni-O-Ni angle. This picture is supported by work examining the antiferromagnetic transition in orthoferrites under pressure.[12] Even though the phase transition in the orthoferrites is an antiferromagnetic one (instead of a MI transition) a similar trend in the Fe-O-Fe angle can be extracted. The antiferromagnetic transition temperature T_N increases with increasing pressure for $R FeO_3$ materials, while T_N at ambient pressure decreases across the rare-earth series.[13] This can be viewed in a similar light as the $R NiO_3$ series. The superexchange interaction, as well as the electronic bandwidth, decreases with decreasing M-O-M (M=magnetic transition metal) angle.[14] As the Fe-O-Fe bond angle decreases across the rare-earth series, the superexchange interaction decreases, resulting in the reduction of T_N. The results of applied pressure, increasing T_N with increasing pressure, indicate that pressure tends to straighten the Fe-O-Fe bond. This crystallographic change under pressure can be expected to be universal in any $R MO_3$ orthoferrite structure.

The above analysis assumes that the sole effect of pressure is to broaden the oxygenlike band and therefore lower T_{MI}. This overlooks the possibility of the bands themselves (the size of the charge-transfer gap) being pressure dependent. One way of addressing this issue would be to perform elastic neutron diffraction under pressure and determine the atomic positions as a function of pressure. This would allow for an examination of the pressure dependence of the Ni-O-Ni bond angle, as well as give the necessary bond lengths for an estimation of band-structure parameters, such as the Hubbard U, bandwidth t, and charge-transfer gap Δ. Such measurements could also examine the temperature and pressure dependence of Jahn-Teller-like distortions.[15]

In summary, we have presented data on the pressure dependence of the first-order MI phase transition found in the charge-transfer-gap compounds $NdNiO_3$ and $PrNiO_3$. The MI transition is extremely pressure sensitive, especially in $PrNiO_3$, which has its T_{MI} suppressed from 130 K to below 1.5 K by 14.1 kbar of applied pressure. Analysis of the T_{MI}-pressure phase diagram within the charge-transfer-gap framework outlined by Torrance *et al.*[4] leads to the prediction that a pressure induced increase in the Ni-O-Ni angle (or the tolerance factor) is responsible for the changes in T_{MI}. This conclusion is supported by earlier work examining the pressure dependence of the Néel temperature of orthoferrites under pressure.[12]

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[15] The focus of this paper has been to analyze the implications of $\rho(T,P)$ data within the framework of the charge-transfer-gap model. Another possible mechanism for the MI transition that has been suggested by T. M. Rice is that the low-temperature insulating ground state is due to a Jahn-Teller-like distortion splitting the $\frac{1}{4}$-filled Ni^{3+} band into a $\frac{1}{2}$-filled band. This $\frac{1}{2}$-filled band could then undergo a transition into a Mott-insulating ground state at lower temperatures. Structural refinement of the atomic positions at low temperatures and high pressures would help address this possibility.