

Possible common ground for the metal-insulator phase transition in the rare-earth nickelates $R\text{NiO}_3$ ($R=\text{Eu, Ho, Y}$)

Fernando P. de la Cruz

Laboratorio Nacional de Investigación y Servicios en Espectroscopía Óptica, Centro CEQUINOR, Departamento de Química, Universidad Nacional de La Plata, Casilla de Correo 962, 1900 La Plata, Argentina

Cíntia Piamonteze

Laboratório Nacional de Luz Síncrotron, Caixa Postal 6192, 13083-970 Campinas, São Paulo, Brazil and Instituto de Física, Universidade Estadual de Campinas, 13083-970 Campinas, São Paulo, Brazil

Néstor E. Massa*

Laboratorio Nacional de Investigación y Servicios en Espectroscopía Óptica, Centro CEQUINOR, Departamento de Química and Departamento de Física, Universidad Nacional de La Plata, Casilla de Correo 962, 1900 La Plata, Argentina

Horacio Salva

Comisión Nacional de Energía Atómica, Centro Atómico Bariloche and Instituto Balseiro, 8400 Bariloche, Rio Negro, Argentina

José Antonio Alonso, María Jesús Martínez-Lope, and María Teresa Casais

Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Cantoblanco, E-28049 Madrid, Spain

(Received 22 April 2002; published 30 October 2002)

We report on the infrared spectra of $R\text{NiO}_3$ ($R=\text{Eu, Ho, Y}$). They provide evidence of phonon and insulating gap behavior and point to the monoclinic distortion at the metal-insulator (MI) transition as a feature for all $R\text{NiO}_3$ ($R\neq\text{La}$). We hypothesize that the intermediate paramagnetic phase (above T_N and below T_{MI}) in $R\text{NiO}_3$ ($R=\text{Sm, Eu, Ho, Y}$) might be consequence of a self-doping effect, gradually triggering a phase segregation in electron-rich and electron-poor regions. This picture is concomitant to the temperature-dependent effect of octahedral tilting and distortion and self-trapped electrons in a polaronic medium.

DOI: 10.1103/PhysRevB.66.153104

PACS number(s): 78.30.Er, 71.30.+h

Rare-earth nickelate $R\text{NiO}_3$ perovskites have triggered a great deal of interest among solid-state chemists and physicists due to the still not well understood phenomena related to their anomalous magnetic ordering and the metal-insulator (MI) transitions they experience as a function of temperature and the rare-earth size. $R\text{NiO}_3$ ($R\neq\text{La}$) have been described as orthorhombically distorted perovskites (space group $Pbnm$), the structure of which was unchanged in all the temperature regime; nevertheless, recent high-resolution neutron and synchrotron x-ray studies demonstrated the presence of a low-symmetry-low-temperature phase characterized by a charge disproportionation effect describable in the monoclinic $P2_1/n$ space group below T_{MI} .¹ This change of symmetry concomitant with T_{MI} was only observed for the smaller rare-earth members of the $R\text{NiO}_3$ family, $R=\text{Y, Ho, ..., Lu}$ (Ref. 1), and only very recently in NdNiO_3 thin films.²

All the $R\text{NiO}_3$ ($R\neq\text{La}$) perovskites experience an antiferromagnetic ordering below T_N , which coincides with T_{MI} for the larger members of the series ($R=\text{Pr, Nd}$).³

It has been puzzling for a long time the reason why the onset of a low-temperature antiferromagnetic ordering at T_N for the smaller rare-earth nickelates ($R=\text{Sm, ..., Lu, Y}$) seems to have no correlation with the change in conductivity at the temperature T_{MI} , in which the metal-insulator phase transition takes place. These oxides experience a sequence of two phase transitions from a (high- T) paramagnetic conducting to a (low- T) insulating antiferromagnetic regime in

which T_{MI} and T_N are ~ 200 K apart by an intermediate paramagnetic insulating state. Below T_{MI} , a charge-transfer gap is open as an excitation gap from O $2p$ to the Ni $3d$ states. Depending on the R ionic size in $R\text{NiO}_3$ ($R\neq\text{La}$) governing the charge-transfer integral between O $2p$ and Ni $3d$ orbitals, the crossover between metallic and semiconducting behavior in the context of the Zaanen-Sawatzky-Allen scheme is reached at temperatures between 350 K ($R=\text{Sm}$) and 600 K ($R=\text{Lu}$).⁴

Electron-phonon interactions are explicit at frequencies close to longitudinal-optical modes, and in addition, infrared reflectivity put in evidence small polaron hopping conductivity yielding the typical tail of metal oxides.⁵ Strong electron-lattice interaction was further verified by the unusually large isotopic shifts of the metal-insulator transition [$T_{\text{MI}}(^{18}\text{O}) - T_{\text{MI}}(^{16}\text{O}) \sim 10$ K] found by Medarde *et al.*⁶ Neutron-diffraction measurements show that there is a linear relation between the metal-insulator transition and the tilting angle of the NiO_6 octahedra.^{6,7}

Here we report on the temperature-dependent infrared activity of $R\text{NiO}_3$ ($R=\text{Eu, Ho, Y}$) with T_{MI} at ~ 483 , ~ 573 , and ~ 582 K and T_N at ~ 205 , ~ 145 , and ~ 138 K, respectively.⁸

Infrared transmission and reflectivity measurements have been done using facilities and techniques already reported.⁵ To assure stabilization of Ni^{3+} cations in smaller rare-earth nickelates, $R\text{NiO}_3$ ($R=\text{Pr, Nd, Sm, Eu}$) were prepared at

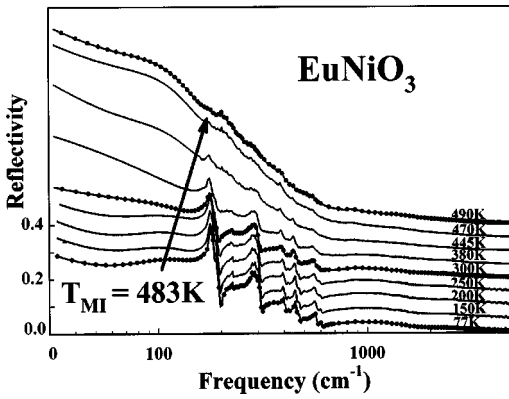


FIG. 1. Infrared reflectivity of EuNiO_3 . A full line represents experimental measurements and the dots represent reflectivity obtained by dielectric simulation. The spectra have been vertically displaced for better viewing.

1000 °C under high pressure up to 200 bars.⁹ HoNiO_3 and YNiO_3 , requiring a more oxidizing synthesis, were prepared in a piston-cylinder press. These procedures yielded black, well-crystallized powders, and in the case of EuNiO_3 , pellets suitable for reflectivity. We stress that throughout these measurements we used fresh samples to avoid Ni^{2+} reduction due to superficial hydroxidation or carbonation.

Phonon frequencies and optical conductivity as well as the overall temperature-dependent reflectivity of EuNiO_3 , Fig. 1, mirror those for SmNiO_3 where lower symmetry was detected in the insulating phase.⁵ Close to T_{MI} the electron-phonon interaction becomes evident as antiresonances due to self-trapped electrons near longitudinal-optical frequencies in polarizable oxygen bonds. At about 300 K the number of phonon bands, shown for transmission in Fig. 2(a), signal that a lower than orthorhombic lattice distortion has taken place. Infrared small polaron conductivity, as for other reported nickelates,⁵ yields at low temperatures high η values, a parameter characterizing the strength of the electron-phonon interaction, while approaching $T_{\text{MI}} \sim 483$ K smaller η values are obtained.

Since the Ni^{3+} stabilization in HoNiO_3 and YNiO_3 requires the internal oxygen pressure generated *in situ* by the decomposition of KClO_4 (giving $\text{KCl} + 2\text{O}_2$) (Ref. 8), as-grown pellets prepared for reflectivity measurements were contaminated by KCl as an undesired impurity, and thus, unsuitable for quantitative reflection measurements. Nevertheless, once the as-grown pellets were ground and the resulting powder was washed in aqueous HNO_3 (to dissolve KCl and eliminate unreacted NiO and R_2O_3), the polycrystalline nickelates were stable and, as Figs. 2(b) and 2(c) show, standard transmission procedures yielded excellent spectra. Phonon bands in the absorption mode, Fig. 2, have the overall temperature dependence reported elsewhere for other nickelates.⁵ And again, the signature of the monoclinic distortion is observed below T_{MI} . We also note that infrared-absorption spectra are proportional by a frequency-dependent factor to the infrared conductivity.¹⁰ The emerging gap similar to other perovskite oxides,¹¹ here with a somehow better defined $e_g \rightarrow t_{2g}$ band centered at ~ 4000 cm^{-1} for

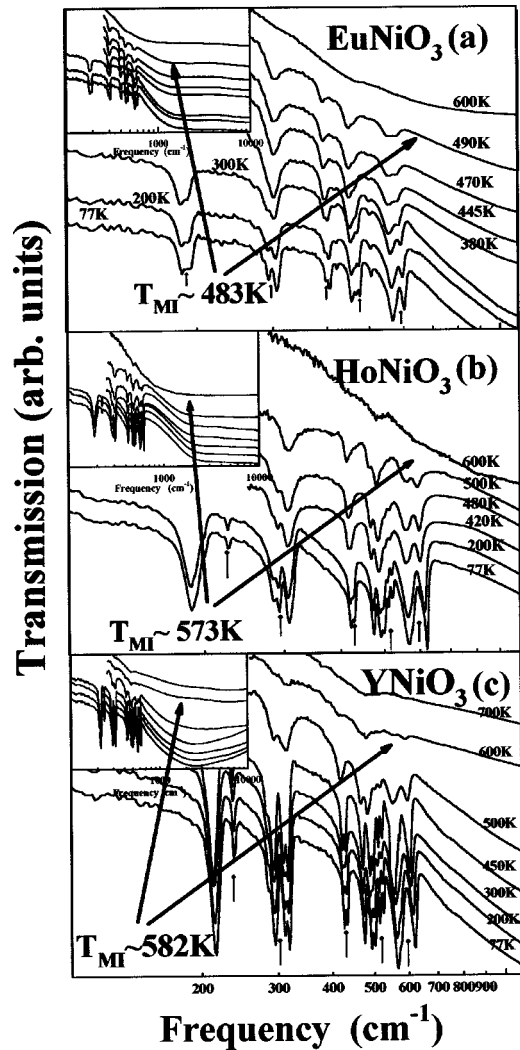


FIG. 2. (a) Infrared transmission phonon spectra of EuNiO_3 between 77 and 600 K; (b) *ibidem* HoNiO_3 ; (c) *ibidem* YNiO_3 between 77 and 700 K. The insets show the overall behavior between 40 and 10000 cm^{-1} . Arrows signal bands modified by the monoclinic distortion. The higher temperature far-infrared transmission measurements were limited up to 400 K because pellets used in that spectral region are made of polyethylene. The spectra have been vertically displaced for better viewing.

YNiO_3 , Fig. 2(c), does not have traces near its edge (~ 94 $\text{meV} = 752$ cm^{-1} at 77 K, 0.25-meV resolution) of subtle substructures close to T_N that might be associated with an onset of antiferromagnetic ordering.

The consequence of a monoclinically distorted $P2_1/n$ lattice in EuNiO_3 , YNiO_3 , and HoNiO_3 is the existence of two crystallographically independent nickel sites and three kinds of nonequivalent oxygen atoms where each NiO_6 octahedra is linked to six Ni_2O_6 octahedra. We have already reported that the amplitudes of Fourier transform of extended x-ray absorption fine structure (EXAFS) oscillations, i.e., the pseudoradial distribution functions, reveal that this finding may be extended to the large rare-earth members RNiO_3 ($R = \text{Pr}, \text{Nd}$) as a small departure from the orthorhombic symmetry. This implies either a distortion in the NiO_6 octahedra

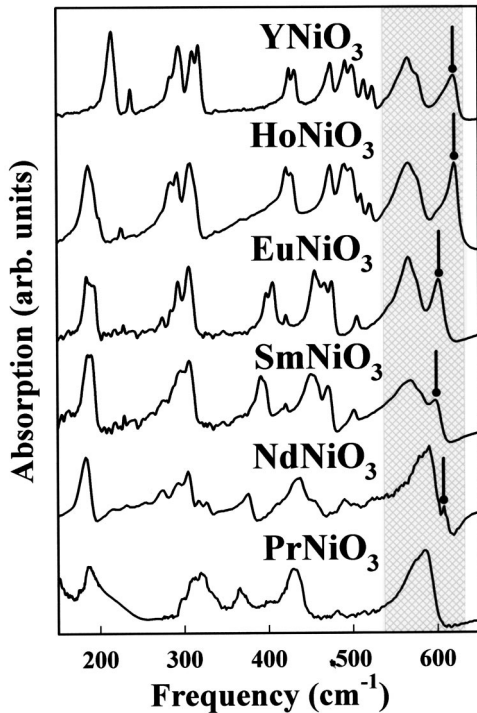


FIG. 3. Lattice absorption spectra of $RNiO_3$ ($R \neq La$) at 77 K.

(identifiable with a Ni Jahn-Teller distortion) or that there are two different Ni sites in the insulating phase.¹² This, in turn, distinctively points to a structurally lower symmetry near and below T_{MI} that correlates well with charge disproportionation as a more subtle monoclinic distortion for the *larger* rare-earth perovskites. The reported orthorhombic space group for $EuNiO_3$ above, but near, T_{MI} would be consequence of averaging in the neutron-diffraction analysis.¹²

In Fig. 3 nickelate phonon bands at 77 K are shown as a function of the rare earth sequencing the degree of structural distortion. Octahedral breathing modes at ~ 600 cm^{-1} are the vibrations that are being more affected by octahedral tilting and shape, i.e., the $O_{2p}-Ni_{3d}$ hybridization, and have bands where the overall multiplicity is better depicted. Note that the least distortion, in accordance with Piamonteze *et al.*,¹² is for $PrNiO_3$, where there is only a main band asymmetry and not an explicit phonon splitting. We do not observe a two-group separation as in susceptibility measurements.

We then suggest that all $RNiO_3$ ($R \neq La$) share a common triggering mechanism of the metal-insulator phase transition related to octahedral tilting and distortion and to self-trapped electrons in a polaronic medium. Similarly, we infer that spin ordering *per se* is not a good order parameter in simple nickelates. This conclusion is strongly supported by recent independent measurements by electron diffraction and Raman scattering. It is reported that the metal-insulator phase transition in $NdNiO_3$ thin films is associated with important structural and vibrational changes at T_{MI} described by a $Pbnm$ to $P2_1/n$ lattice phase transition.¹³ And, as it was pointed out above, charge order in $NdNiO_3$ films had been observed at the metal-insulator transition using resonant x-ray scattering implying a long-range ordered ground state with two distinct Ni sites, $Ni^{3+\delta}$ and $Ni^{3-\delta'}$, with $\delta + \delta' = 0.42 \pm 0.04e$ (Ref. 2).

The driving force for the monoclinic distortion leading to two independent positions for Ni is also ordering between two differently charged Ni cations for the last six members of the $RNiO_3$ series.^{1,11} In these last ones the insulating phase consists of expanded ($Ni1O_6$) and contracted ($Ni2O_6$) octahedra that alternate along the three directions of the crystal, with evidence of an incomplete stabilization of a charge disproportionation, $2Ni^{3\pm\delta} \rightarrow Ni^{3+\delta} + Ni^{3-\delta}$, a mutual self-doping process, with mean value of $2\delta = 0.6$ electrons;¹ i.e., an incomplete $2Ni^{3+} \rightarrow Ni^{2+}$ ($S=1$) + Ni^{4+} ($S=0$) process.

Thus, a more compatible picture may be proposed for all $RNiO_3$. We conjecture that the unusual spin propagation vector $\mathbf{k} = (1/2, 0, 1/2)$ (Refs. 1 and 14) in a net antiferromagnetic arrangement, the results of alternating nearest-neighbors Ni^{3+} ions in ferromagnetic and antiferromagnetic couplings, and the temperature divorce in T_N and T_{MI} may be a consequence of the triggering of a self-electron-doping effect, leading to the separation between electron-rich and electron-poorer regions. These anomalies near T_{MI} will usher local monoclinic-like lattice malformations with an overall single structural environment. It is known that in oxides, as in $CaMnO_3$, hole doping induces a magnetic transition without a significant variation in the lattice constants,¹⁵ and on going from $LaMnO_3$ to $TbMnO_3$, close to the limit for a distorted perovskite structure, the complexity of the magnetic structure increases as the rare-earth reduces in size.¹⁶ Further, since the onset of antiferromagnetic order in smaller rare-earth nickelates is not sharp, segregation, difficult to detect with x-ray or neutron-diffraction techniques, may play a role in the insulating paramagnetic phase. Paraphrasing findings currently discussed for manganese compounds in the context of electronic mixed phases,¹⁷ different charge densities, and magnetic states are expected to coexist and, in our case, would only consolidate the magnetic order at T_N due to temperature-dependent electron localization that may include Jahn-Teller effects. In $Tb_{0.01}Ca_{0.99}MnO_3$ (Ref. 15), whose resistivity (similar to $NdNiO_3$) has a rather sharp metal-insulator phase transition, spontaneous charge separation induces magnetic separation corresponding to electron-rich and electron-poor microregions.^{16,18} In $RNiO_3$, inhomogeneous regions with charge separation (2δ) and associated net spins close to $S=1$ (Ni^{2+}) and $S=0$ (Ni^{4+}) may only consolidate at $\sim T_N$. Localization, directly observed in infrared reflectivity close to the longitudinal-mode frequencies (e.g., Fig. 1), is a gradual effect heavily dependent on the temperature. Then, space inhomogeneities, influencing spin order, may be thought as the common feature with a more subtle degree of charge separation for the case of larger rare-earth cations. This, in turn, suggests that charge density is the order parameter of the metal-insulator phase transition. As pointed by Vobornik *et al.*¹⁹ for those nickelates in which $T_{MI} \sim T_N$, most of the experimental findings state that T_{MI} is independent of magnetic interactions and we feel that a theoretical approach along mixed phase separation concept may help in bringing together the apparent unlike behavior in the $RNiO_3$ ($R \neq La$) family. It also calls for increasing experimental resolution of neutron, x-ray (i.e., techniques dealing with long-range ordering) photoemission measurements to clear the understanding of the overall picture of these fascinating compounds.

Note added. We recently became aware of a publication by Yamamoto and Fujiwara [J. Phys. Chem. Solids **63**, 1347 (2002)] with calculations relying in older measurements that assign two different crystallographic space groups for NdNiO₃ and YNiO₃, respectively. We believe that under the light of Refs. 2, 12, and 13, as well as the results reported here, their basic hypothesis ought to be revised. We also note that the same observation applies in analyzing the results of

substituting Ni by Fe in a more recent publication by Kim *et al.* [Phys. Rev. B **66**, 014427 (2002)].

J.A.A., M.J. M-L, and M.T.C. acknowledge the financial assistance of the Ministerio de Ciencia y Tecnología under Project No. MAT2001-0539. Also, C.P. acknowledges the financial support of (Grant No. PROC. 00/00789-3) the FAPESP, São Paulo, Brazil, and thanks the CLAF (Centro Latino Americano de Física) for financial support.

*Email address: nem@dalton.quimica.unlp.edu.ar

- ¹J. A. Alonso, M. J. Martínez-Lope, M. T. Casais, J. L. García-Muñoz, and M. T. Fernández-Díaz, Phys. Rev. B **61**, 1756 (2000).
- ²U. Smith, G. I. Meijer, F. Fauth, R. Allemspach, J. G. Bednorz, J. Karpinski, S. M. Kazakov, L. Paolasini, and F. D'Acapito, Phys. Rev. Lett. **88**, 126402 (2002).
- ³For an earlier review, see M. Medarde, J. Phys.: Condens. Matter **9**, 1679 (1997).
- ⁴J. Zaanen, G. A. Sawatzky, J. W. Allen, Phys. Rev. Lett. **55**, 418 (1995).
- ⁵N. E. Massa, J. A. Alonso, M. J. Martínez-Lope, and I. Rasines, Phys. Rev. B **56**, 986 (1997); N. E. Massa, H. Falcon, H. Salva, and R. E. Carbonio, Phys. Rev. B **56**, 10 178 (1997); M. A. Mroginiski, N. E. Massa, H. Salva, J. A. Alonso, and M. J. Martínez-Lope, *ibid.* **60**, 5304 (1999).
- ⁶M. Medarde, P. Lacorre, K. Conder, F. Fauth, and A. Furrer, Phys. Rev. Lett. **80**, 2397 (1998).
- ⁷M. Medarde, J. Mesot, P. Lacorre, S. Rosenkranz, P. Fisher, and K. Gobrecht, Phys. Rev. B **52**, 9248 (1995).
- ⁸J. A. Alonso, M. J. Martínez-Lope, M. T. Casais, J. L. García-Muñoz, M. T. Fernández-Díaz, and M. A. G. Aranda, Phys. Rev. B **64**, 94102 (2001).
- ⁹J. A. Alonso, M. J. Martínez-Lope, and I. Rasines, J. Solid State Chem. **170**, 120 (1995).
- ¹⁰A. Paolone, P. Giura, P. Calvani, P. Dore, S. Lupi, and P. Maselli, Physica B **244**, 33 (1998).
- ¹¹P. Calvani, G. De Marzi, P. Dore, S. Lupi, P. Maselli, F. D'Amore, S. Gagliardi, and S.-W. Cheong, Phys. Rev. Lett. **81**, 4504 (1998).
- ¹²C. Piamonteze, H. C. N. Tolentino, A. Y. Ramos, N. E. Massa, J. A. Alonso, M. J. Martínez-Lope, and M. T. Casais, *Proceedings of the Fifth Latin American Workshop on Magnetism, Magnetic Materials and their Applications*, edited by C. A. Ramos, B. Alascio, M. T. Causa, and M. Tovar [Physica B **320**, 71 (2002)]; C. Piamonteze, H. C. N. Tolentino, F. C. Vicentin, A. Ramos, N. E. Massa, J. A. Alonso, M. J. Martínez-Lope, and M. T. Casais, in *Proceedings of the Thirteenth International Conference on Vacuum Ultraviolet Radiation Physics*, edited by K. C. Prince, G. Comelli, and M. Kiskinova [Surface Rev. Lett. **9**, 1121 (2002)]; N. E. Massa, F. P. de la Cruz, C. Piamonteze, H. Salva, J. A. Alonso, M. J. Martínez-Lope, and M. T. Casais, Bull. Am. Phys. Soc. **46** (1), 149 (2001).
- ¹³M. Zaghrioui, A. Bulou, P. Lacorre, and P. Laffez, Phys. Rev. B **64**, R81102 (2001).
- ¹⁴J. Rodríguez-Carvajal, S. Rosenkranz, M. Medarde, P. Lacorre, M. T. Fernández-Díaz, F. Fauth, and V. Trounov, Phys. Rev. B **57**, 456 (1998).
- ¹⁵Y. Moritomo, A. Machida, E. Nishibori, M. Takada, and M. Sakata, Phys. Rev. B **64**, 214409 (2001).
- ¹⁶J. Blasco, C. Ritter, J. Garcia, J. M. Teresa, J. Pérez-Cacho, and M. R. Ibarra, Phys. Rev. B **62**, 5609 (2000).
- ¹⁷E. Dagotto, T. Hotta, and A. Moreo, Phys. Rep. **344**, 1 (2001).
- ¹⁸J. J. Neumeier and J. L. Cohn, Phys. Rev. B **61**, 14 319 (2000).
- ¹⁹I. Vobornik, L. Perfeti, M. Zacchigna, M. Grioni, G. Margaritondo, J. Mesot, M. Medarde, and P. Lacorre, Phys. Rev. B **60**, R8426 (1999).