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Infrared and Mössbauer Spectroscopic Study of the Metal–Insulator Transition in Some Oxides of Perovskite Structure*

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The IR spectra of some $LaNi_{1-x}B_xO_3$ (B = Cr, Fe, and Co) compounds having perovskite structure have been studied in the range 1000–300 cm^{-1}. An investigation of the changes in the metal–oxygen stretching frequency as $x \rightarrow x_c$ from the insulating side has been carried out. An important feature is that as $x \rightarrow x_c$ the vibrational features in the infrared spectra disappear when the resistivity is $\sim 10^{-1}$ Ω cm which is of two orders of magnitude more than the value of ρ_0 at which the temperature coefficient of resistance changes sign. Mössbauer studies on Fe-containing samples with various conductivities show that the isomer shift decreases as conductivity increases which is indicative of larger Fe–O overlap.

Introduction

We have recently been investigating the metal–insulator (MI) transitions in $LaNi_{1-x}B_xO_3$ (B = Cr^{3+}, Mn^{3+}, Fe^{3+}, and Co^{3+}) solid solutions (*1, 2*). $LaNiO_3$ is known to be metallic while the $LaBO_3$ oxides are magnetic insulators (*3–5*) with well defined magnetic ordering temperatures when B = Cr, Mn, and Fe. The temperature coefficient of resistance (TCR) changes sign in the $LaNi_{1-x}B_xO_3$ solid solutions at a critical value of x_c which depends on the B ion (B = Mn, $0.03 < x_c < 0.05$; B = Cr, $0.05 < x_c < 0.1$; B = Fe, $0.25 < x_c < 0.35$; B = Co, $0.35 < x_c < 0.5$). The compositions with $x < x_c$ are considered to be metallic, TCR being positive. It was of interest to us to obtain information at a microscopic level on the nature of metal–oxygen bonding at the MI transition. Among the techniques that are available are infrared and Mössbauer spectroscopy.

Infrared spectra of ABO_3 perovskite oxides in the region 1000–300 cm^{-1} have been studied by several workers (*6–9*). In general, the ABO_3 perovskites show two prominent bands in this region. The assignment of absorption bands based on factor group analysis in these oxides has not been successful as in the flourides (*9–12*). Fair success has been obtained, however, by considering the internal modes of BO_6 octahedra. The higher $\nu_{B\text{–}O}$ frequency band is usually assigned to a metal–oxygen stretching frequency and the lower frequency band to a deformation mode of BO_6 octahedra. The frequency of these bands has been related to the strength of metal–oxygen covalency (*6*). An investigation of the changes in $\nu_{B\text{–}O}$ in the $LaNi_{1-x}B_xO_3$ solid

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solutions as x approaches x_c from the insulating side was therefore carried out in order to examine the influence of the imminent metalization.

Changes in the Mössbauer isomer shift, δ, of Fe^{57} nuclei in various hosts of different electrical conductivities may also be used as a rough measure of the changes in Fe–O covalency. The relationship between δ and $\nu_{B\text{–}O}$ as well as electrical resistivity ρ was therefore investigated in some La_2FeBO_6 oxides (B = Cr, Mn, Ni). In these oxides the electrical resistivities are $\sim 10^4$, $\sim 10^2$, and $\sim 10^{-1}$ Ω cm at 300 K for B = Cr, Mn, and Ni, respectively. To our knowledge there seems to exist no literature on the correlation between δ and $\nu_{B\text{–}O}$ or ρ. We have examined in some detail changes in the IR spectra of $LaNi_{1-x}B_xO_3$ compounds as $x \rightarrow x_c$ ($x < x_c$).

Experimental

A continuous range of solid solutions of the series $LaNi_{1-x}B_xO_3$ was possible by using low-temperature preparation methods (*13*). The condition of preparation of the samples used in this investigations has been reported earlier (*13*). Infrared spectra were recorded on a Perkin–Elmer 580 spectrometer. A Specac variable temperature cell was used for temperature-dependent studies. The substance (~1 wt%) was mixed thoroughly with dry KBr and pressed into discs of 0.5-mm thickness. Mössbauer spectra were recorded on a homebuilt spectrometer which worked on the constant acceleration mode. The spectral data were processed using a standard least-squares fitting programme MOSFIT. The spectrometer was calibrated against a natural Fe hyperfine spectrum. The isomer shifts given in Table I are with reference to Fe metal.

Results

In Fig. 1 we show the IR spectra obtained from $LaNi_{1-x}Cr_xO_3$. For $x < 0.35$ no feature

TABLE I

PHYSICAL PARAMETERS OF $LaNi_{1-x}B_xO_3$ COMPOUNDS

Compound	a (Å)	CS	$\nu_{B\text{–}O}$ (cm^{-1})	ρ (Ω cm at 300 K)	δ (mm/sec)	γ (mm/sec)	Q · S (mm/sec)
$LaNi_{1-x}Cr_xO_3$							
$x = 1.0$	3.88	O	620	$\sim 10^4$	—	—	—
$x = 0.90$	3.93	C	615	160			
$x = 0.80$	3.89	C	605	30	—	—	—
$x = 0.60$	3.89	C	590	3	—	—	—
$x = 0.50$	3.88	C	590	1.2	—	—	—
$x = 0.35$	3.87	R	590		—	—	—
$LaNi_{1-x}Fe_xO_3$							
$x = 1.0$	3.93	O	560	$\sim 10^7$	0.335		0.04
$x = 0.90$	3.93	C	565	3600			
$x = 0.75$	3.91	C	570	3.6			
$x = 0.5$	3.88	C	575	0.047	0.254	0.31	
$LaNi_{1-x}Co_xO_3$							
$x = 1.0$	3.82	R	600	30	—		
$x = 0.95$	3.83	R	595	10	—		
$x = 0.90$	3.83	R	590	0.07	—		
$LaFe_{0.5}Mn_{0.5}O_3$	3.89	O	605	220	0.297	0.292	0.489
$LaFe_{0.5}Cr_{0.5}O_3$	3.90	O	590	$\sim 10^7$	0.335	0.396	
$LaFe_{0.5}Co_{0.5}O_3$	3.88	R	605	$\sim 10^3$			
$LaNiO_3$	3.84	R		1.6×10^{-3}			

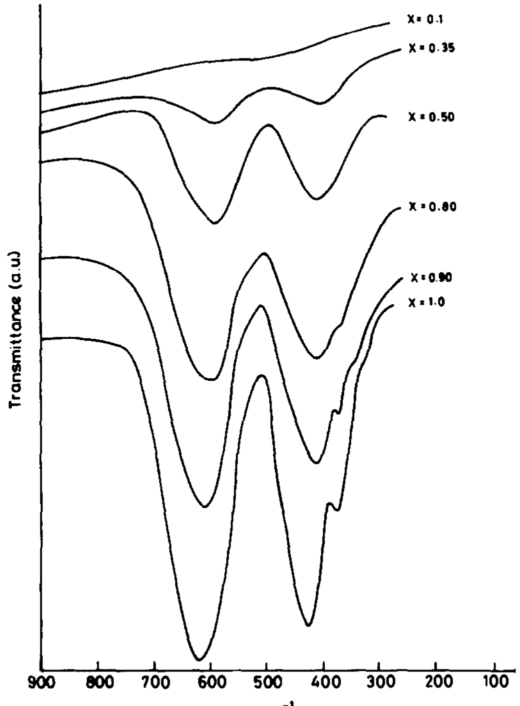

FIG. 1. IR spectra of $LaNi_{1-x}Cr_xO_3$ as a function of x at 300 K.

characteristic of localized vibrational modes is seen, although $x < x_c$ and the sample is semiconducting. This is typical of the $LaNi_{1-x}B_xO_3$ compounds, the vibrational features disappearing at room temperature at a value x' which is less than x_c. It is seen that $\nu_{B\text{–}O}$ decreases with increasing x. This is, however, not typical. In the case of $LaNi_{1-x}Fe_xO_3$, for example, the opposite trend is observed. In Fig. 2 we show the variation of $\nu_{B\text{–}O}$ with x for various B ions. The actual values of $\nu_{B\text{–}O}$ at 300 K for the $LaNi_{1-x}B_xO_3$ and the La_2FeBO_6 compounds are given in Table I along with the values of the resistivity, ρ, the pseudocubic lattice parameter, a, and the crystal symmetry, CS. It is seen from Fig. 2 and Table I that as x approaches x' the B–O stretching frequency approaches a common value between 580 and 590 cm^{-1} shown by shaded region. There seems to be no correlation between a and $\nu_{B\text{–}O}$. The observed $\nu_{B\text{–}O}$ roughly corresponds to the appropriate weighted average value of the individual stretching frequencies $\nu_{B\text{–}O}$ and "$\nu_{Ni\text{–}O}$" if it is assumed that "$\nu_{Ni\text{–}O}$" is around 580–590 cm^{-1}. In the insulating La_2FeBO_6 system (B = Cr, Mn), $\nu_{B\text{–}O}$ is very close to the average stretching frequency of $LaBO_3$ and $LaFeO_3$.

In Fig. 3 we have plotted the variation of log ρ at 300 K as a function of x for $LaNi_{1-x}B_xO_3$ compounds. The dotted line in Fig. 3 joins the approximate values of x' for various B ions, when $x < x'$ where no features due to localized modes are seen in the IR spectra. Apparently a resistivity of $\sim 10^{-1}$ Ω cm leads to disappearance of features in the IR spectra. In order to check this we have carried out a study of the temperature dependence of the IR spectra of $LaCoO_3$. The changes in the IR spectra as a function of temperature are shown in Fig. 4. The vibrational features disappear around 575 K at which temperature the resistivity is $\sim 8 \times 10^{-2}$ Ω cm. A detailed analysis of the IR spectra in this region in which the absorption is due to both charge carriers and localized phonon modes is perhaps

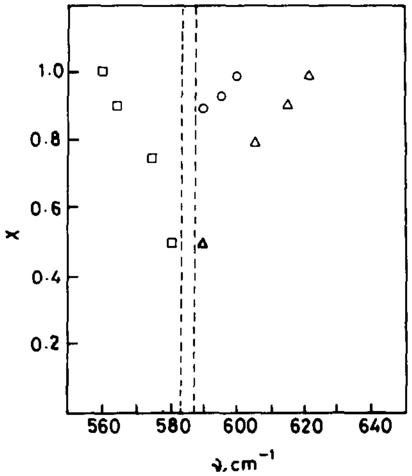

FIG. 2. Variation of $\nu_{M\text{–}O}$ as a function of x at 300 K for $LaNi_{1-x}B_xO_3$ compounds. □, B = Fe; ○, B = Co; △, B = Cr.

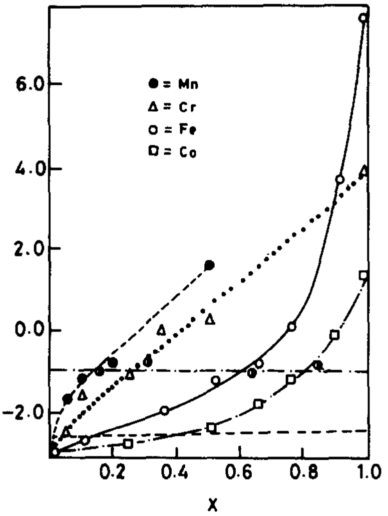

FIG. 3. Log ρ vs x at 300 K for $LaNi_{1-x}B_xO_3$ compounds. Full line indicates values at which $d\rho/dt$ changes sign. Half-filled circles indicate extrapolated value of x' at which vibrational features of IR spectra disappear.

possible, especially with respect to the frequency-dependent conductivity in the polaron or band models (*14–16*). We are currently studying the infrared reflectance data on these samples and the results will be reported in a later communication.

In Fig. 5 Mössbauer spectra of the La_2FeBO_6 compounds (B = Cr, Mn, Ni) are shown. The data in the case of La_2FeNiO_6 and La_2FeCrO_6 have been fitted to singlets although reasonable linewidths are obtained when the fit is made to a quadrupole split line. The quadrupole splitting in both the case is close to 0.04 mm/sec which is in reasonable agreement with the splitting found in $LaFeO_3$. The quadrupole splitting is most pronounced when B = Mn which is to be expected as the Mn^{3+} ion is a Jahn–Teller ion. A comparison of δ with ρ shows that δ decreases with decreasing ρ. δ does not shown any correlation with lattice parameters or $\nu_{M\text{–}O}$ (see Table I).

Discussion

In the $LaBO_3$ compounds (B = V, Cr, Mn, Fe, Co) the oxidation state, mass, and

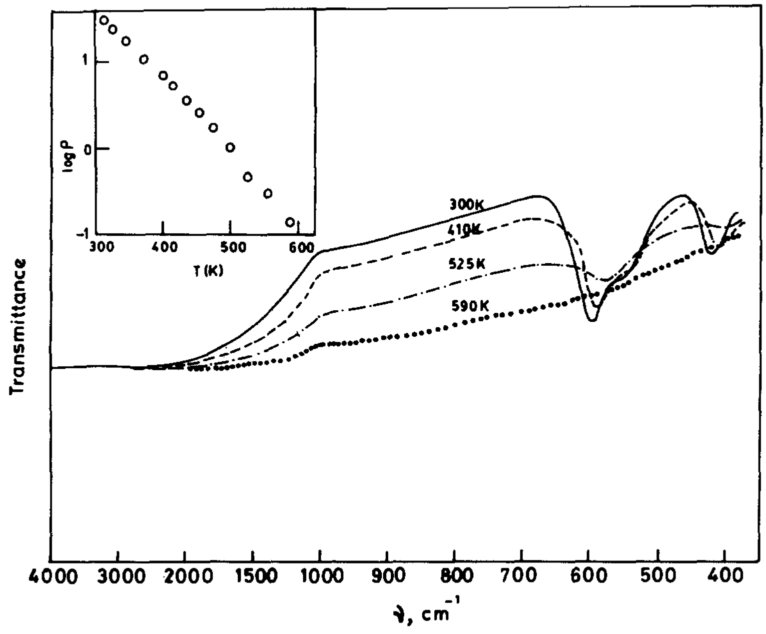

FIG. 4. IR spectra at various temperatures for $LaCoO_3$. Inset shows variation of log ρ as a function of temperature.

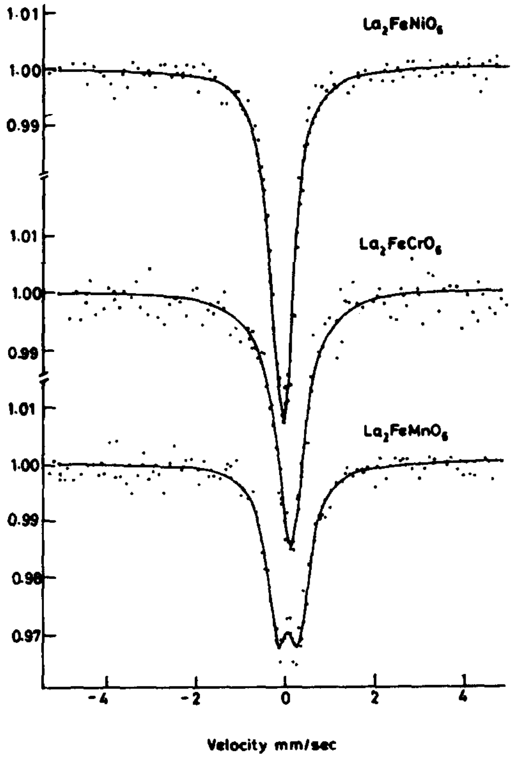

FIG. 5. Mössbauer spectra of La_2FeBO_6 compounds (B = Cr, Mn, Ni) at 300 K.

the ionic radius of the B ions are nearly the same. Yet there is a fairly large range of variation in the stretching frequencies (620–560 cm^{-1}). The lower stretching frequency of $LaFeO_3$ (~560 cm^{-1}) compared to that (620 cm^{-1}) in $LaCrO_3$ is not anticipated in terms of covalent mixing of cation and anion electron wavefunctions as the e_g electrons in the Fe^{3+} are expected from strong σ bonding with anion p_σ orbitals. This anomaly may be resolved if we consider instead the bond order. In the schematic energy level diagram of ABO_3 perovskites (*3*, *4*) the e_g electrons are in antibonding orbitals and hence the bond order would decrease with increase in the number of e_g electrons. This accounts for the observed decrease in the stretching frequency in order ν_{Cr-O} (620 cm^{-1}) > ν_{Mn-O} > ν_{Fe-O} but not the low stretching frequency (~560–570 cm^{-1}) in $LnVO_3$ compounds (*16*).

Since we are considering infrared active modes of BO_6 octahedra involving an off-center displacement of the B ions, large octahedral field stabilization energies Δ_{oct} could lead to higher stretching frequencies. Consideration of Δ_{oct} values listed by McClure (*17*) also accounts qualitatively for the observed trends in the stretching frequency in $LaBO_3$ compounds, except again for $LaVO_3$. On the other hand there is a remarkably good correlation between the octahedral site preference energy (over that of tetrahedral sites) being almost linearly related to the stretching frequency in $LaBO_3$ and B_2O_3 compounds (Fig. 6). A rationale for this correlation may perhaps be obtained if it is assumed that the off-center optic mode displacement takes the cations toward a more tetrahedral coordination.

In the $LaNi_{1-x}B_xO_3$ compounds the trend of the ν_{M-O} values approaching a common value of 580–590 cm^{-1} as x approaches x' although the parent compounds (x = 1.00)

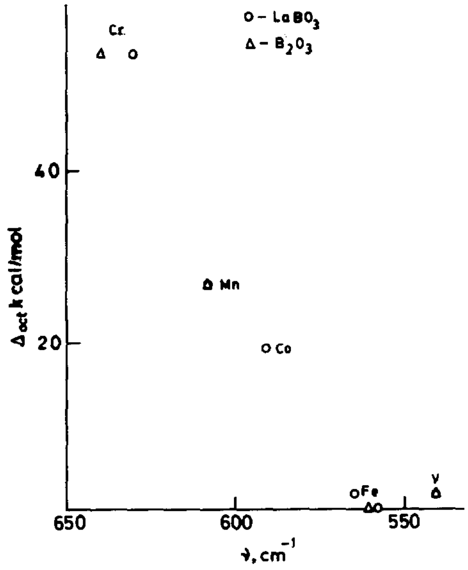

FIG. 6. ν_{M-O} versus octahedral site preference energy Δ, for $LaBO_3$ and B_2O_3 compounds.

could have higher or lower frequencies is in agreement with the bond order model in as much as $\nu_{M\text{-}O} > \nu_{B\text{-}O}$ when the number of e_g electrons is decreased (as when B = Fe). The metallization is not accompanied by a universal decrease or increase in bond order despite large changes in conductivity. The force constant thus seems to be dominated by the ionic component of the bonding and is insensitive to changes in the electron transfer or covalent mixing. This is in agreement with estimates of d electron bandwidth being less than 0.1 eV in the insulating phases compared to the lattice energies of few electron volts per mole (*18*). Mössbauer results on the other hand clearly show that increase in conductivity in La_2FeBO_6 compounds (B = Cr, Mn, or Ni) leads to a decrease in isomer shift, δ, indicating an increase in cation–anion ds mixing as the conductivity increases. The absence of any correlation between $\nu_{(Fe,B\text{-}O)}$ and conductivity or δ again suggests that the force constant associated with B–O in the insulating composition is dominanted by ionic bonding considerations.

The most prominent feature as $x \rightarrow x'$ is the decrease in the intensity of vibrational modes. In this region the absorption coefficient is determined by both charge carriers and the localized modes. The present data, obtained from powder is not suitable for the analysis of optical data in terms of either the band model or the polaron model. We feel, however, that the fact that the vibrational modes disappear when the resistivity approaches 10^{-1} Ω cm could be important. Although the disappearance can be qualitatively attributed to the number of charge carriers, we are not aware of any model based on band picture which would account quantitatively for the disappearance of the vibrational features, when the resistivity decreases to $\sim 10^{-1}$ Ω cm. However, the lower limit of the resistivity in the small polaron model is about 10^{-1} Ω cm as discussed by Frohlich (*19*) and Bosman and Van Daal (*20*). This value of ρ corresponds to the situation when the residence time τ ($\sim 10^{-12}$ sec) of charge carriers at a site is just greater than the lattice vibrational period τ_0 ($\sim 10^{-13}$ sec). When τ becomes comparable to or less than τ_0 a localized vibrational mode may not be defined as during the time of the number of electrons at a site changes. τ itself is expected to decrease as the cation–anion–cation overlap integral b increases if we assume that $\tau = \hbar/W$ where W is the band width and $W = 2zb$ in the tight binding approximation. Indeed a $\tau \approx 10^{-12}$ sec would give a very small band width ($W \sim 10^{-3}$ eV) so that such an exchange would not be expected to contribute significantly to the binding energy and thus the force constant. The cation–anion–cation exchange E_{ex} may be related to frequency, ν, of electron transfer through $E_{ex} = h\nu$ in the manner of Zener (*21*). As the metallic phase is approached ν is expected to increase and τ to decrease. When $\tau \ll \tau_0$ the electrons may be considered to be free, so that we put $\tau \approx 10^{-14}$ sec as the criterion for the metallic behavior. At the boundary of the metal–insulator transition, the relaxation time in the metallic phase is expected to be a minimum value τ_{min}. Equating τ_{min} to 10^{-14} sec we obtain a value for $\sigma_{min} = ne^2\tau/m^* = 5 \times 10^2\ \Omega^{-1}\ cm^{-1}$ when $m^* \approx 10m$. A value of $m^* \approx 10m$, near the MI transition has been obtained for $La_{1-x}Sr_xVO_3$ from the photoelectron studies (*22*) and is in agreement with magnetic susceptibility data also (*18*).

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