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# Pressure-induced charge transfer in lanthanum nickel ferrate ( $\text{LaNi}_{0.5}\text{Fe}_{0.5}\text{O}_3$ ) and analogies to composition-driven charge transfer in dilanthanum cuprate ( $\text{La}_2\text{CuO}_4$ ): an infrared study

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**Abstract.** A reversible pressure-induced phase transition in lanthanum nickel ferrate ( $\text{LaNi}_{0.5}\text{Fe}_{0.5}\text{O}_3$ ) manifests itself in the infrared spectrum of the transition metal–oxygen stretching ( $\nu_{\text{TM-O}}$ ) modes by the emergence of new peaks at pressures greater than  $\sim 1.4 \times 10^9$  Pa. Analogies to this transition are made by considering charge transfer in dilanthanum cuprate ( $\text{La}_2\text{CuO}_4$ ) and its modification by partial substitution of copper ions by chromium ions.

## 1. Introduction

Lanthanum transition metallates ( $\text{LaTMO}_3$ —where TM is a transition metal) demonstrate a wide variety of electrical and magnetic properties which have been shown to depend upon the spin state of the transition metal ion [1]. Low-spin lanthanum transition metallates exhibit semiconducting to metal phase transitions [2] or are metallic at all measured temperatures whereas high-spin lanthanum transition metallates are insulators [1]. Although the electronic properties of the lanthanide transition metallates are quite varied, they have very similar crystallographic structures based upon a cube, although frequently there are slight distortions away from perfect cubic symmetry mostly to rhombohedral or orthorhombic symmetry. It is found that the electrical properties of these materials are closely allied to the crystallographic structure. Materials with metal-like properties or those with relatively low resistivities are almost always cubic or rhombohedral whereas the insulators or poor semiconductors tend to possess orthorhombic crystallographic symmetry. This is certainly the case for the lanthanum nickel ferrate ( $\text{LaNi}_x\text{Fe}_{1-x}\text{O}_3$ ) system which is reported [3] to undergo a change from an orthorhombic to cubic system when  $x$  is greater than 0.1. Also, the resistivity [3] of these compounds decreases as  $x$  increases ( $\sim 10^7$ ,  $3.6 \times 10^3$ , 3.6 and  $47 \times 10^{-3} \Omega \text{ cm}$  for  $x = 0, 0.1, 0.25$  and 0.5, respectively). In contrast,  $\text{La}_2\text{TMO}_4$  materials adopt the  $\text{K}_2\text{NiF}_4$  structure which can be considered as an ordered intergrowth of perovskite-like  $\text{LaTMO}_3$  and  $\text{LaO}$  rocksalt layers stacked along the crystallographic  $c$ -axis. Because of the layered nature of these materials, the electronic properties [4] tend to be anisotropic.

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Lanthanum transition metallates are also quite unusual in that they can stabilize ions in comparatively high oxidation states, for example  $\text{LaNiO}_3$  with nickel in the trivalent state. Mixed valency in these systems can also be found. The Mössbauer spectra of solid solutions of  $\text{Sr}_{1-x}\text{La}_x\text{FeO}_3$  and  $\text{Ca}_{1-x}\text{Sr}_x\text{FeO}_3$  led Takano *et al* [5] to suggest that the disproportionation  $2\text{Fe}^{4+} = \text{Fe}^{(4-\lambda)+} + \text{Fe}^{(4+\lambda)+}$  ( $0 \leq \lambda \leq 1$ ) is more correctly described using non-integral charges. Battle *et al* [6] have shown that in  $\text{Sr}_2\text{LaFe}_3\text{O}_{8.94}$  there exists both a commensurate charge density wave (CDW) and commensurate spin density wave (SDW) propagating along the [111] axis of the crystal and that charge disproportionation (in idealized  $\text{Sr}_2\text{LaFe}_3\text{O}_9$ ) can be described as  $3\text{Fe}^{3.66} = 2\text{Fe}^{3+} + \text{Fe}^{5+}$ . Studies on nickel-containing analogues are less well documented. The work of Benloucif *et al* [7] on  $\text{La}_{2-x}\text{Sr}_x\text{Ni}_{1-y}\text{Fe}_y\text{O}_{4-(x-y)/2+\delta}$  suggested that in these materials—formally—nickel is in the lower divalent oxidation state and that the iron ions exist in the tetravalent state, as well as both iron and nickel existing in the trivalent state. In the study by Takeda *et al* [8] of  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ , effort was made to maintain stoichiometric oxygen content. In these materials, the average oxidation state of the nickel can vary between 2 and about 3.4. Most interestingly, in the interval  $0 \leq x \leq 0.6$ , there is a slight gradual displacement of one of the oxygen atoms (O(2) in their notation) which controls localized-electron to itinerant-electron behaviour. Most importantly, in  $\text{La}_2\text{CuO}_4$  partial substitution of lanthanum by divalent cations, barium [9] for example, can lead to materials with superconducting properties.

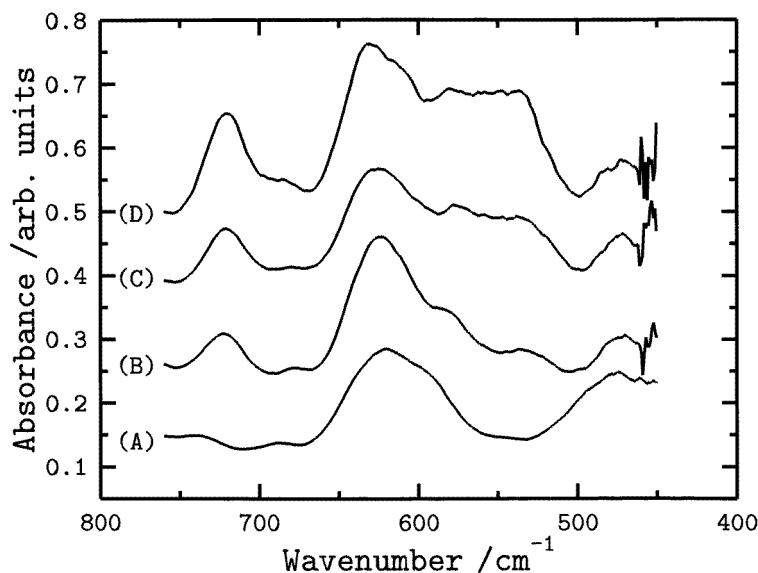
The principal question which we address in this paper is whether electron (charge) transfer between dissimilar transition metal ions can be controlled without change of chemical composition; in this instance by the use of pressure variation. This is the case, for example, with  $\text{Cs}_2\text{Au}_2\text{Cl}_6$  [10] where there is a change from formal  $\text{Au}^I + \text{Au}^{III}$  to  $2\text{Au}^{II}$  species at about  $6 \times 10^9$  Pa. We shall draw analogies to charge transfer in dilanthanum cuprate and its restriction by the partial substitution of copper ions by ‘electronically insulating’ chromium ions.

## 2. Experimental details

The preparation of lanthanum nickel ferrates and analytical procedures have been reported in a previous publication (reference [13] of [3]).  $\text{La}_2\text{CuO}_4$ ,  $\text{La}_2\text{Cr}_{0.5}\text{Cu}_{0.5}\text{O}_4$  and  $\text{LaCrO}_3$  were prepared by thermal decomposition of the appropriate solution of metal nitrates (Aldrich Chemical Company, purity 99.9% or greater). This was followed by thermal annealing in air at 1120 K for sixteen hours followed by cooling at  $1 \text{ K min}^{-1}$ . X-ray diffraction patterns were obtained with a home-built powder diffractometer using and position sensitive detector: silicon was used as a standard. The x-ray diffraction patterns were in agreement with published data as were their vibrational spectra with the exception of  $\text{La}_2\text{Cr}_{0.5}\text{Cu}_{0.5}\text{O}_4$  for which there were no literature data available to us. The x-ray diffraction pattern, however, did indicate a monophasic material with a  $\text{K}_2\text{NiF}_4$ -like structure. Infrared spectra were collected using a Nicolet 740 spectrometer. For variable-pressure measurements, a mercury cadmium telluride (MCT) detector cooled to 77 K was used. A diamond anvil cell using gaskets with apertures of  $\sim 350 \mu\text{m}$  was used to apply an external pressure. The samples were incorporated into sodium bromide (99.99%, Aldrich Chemical Company) which contained 0.3% w/w sodium nitrite (97%, Aldrich Chemical Company) as internal pressure calibrant [11, 12]. All measurements were carried out at an ambient temperature of  $\sim 295 \text{ K}$  and pressure  $\sim 0.1 \times 10^6 \text{ Pa}$  unless otherwise stated. Materials measured under ambient conditions were suspended in potassium bromide matrices and a deuterated triglycine sulphate infrared detector was used.

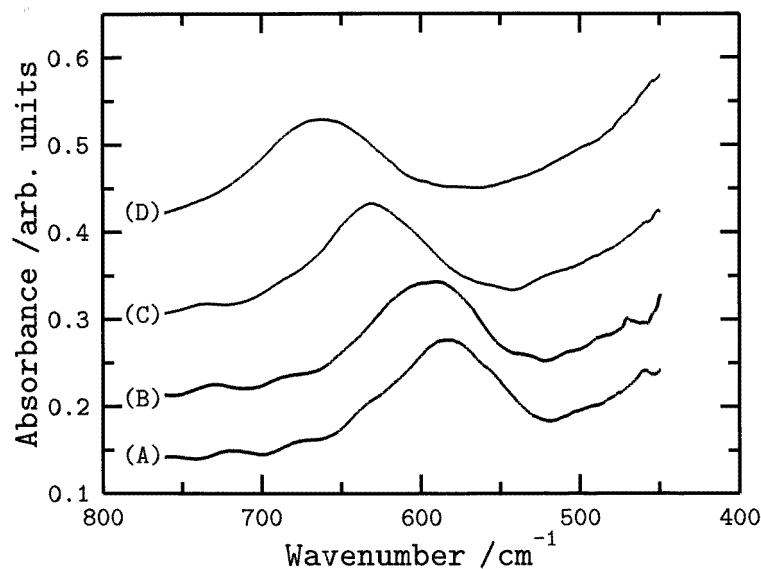
### 3. Results

We have established that there is anomalous pressure-dependent behaviour in the lanthanum nickel ferrates  $\text{LaNi}_x\text{Fe}_{1-x}\text{O}_3$  with  $x$  ranging from about 0.4 to 0.7 and at approximately the same pressure. In the composition range  $x = 0$  to 0.3 there is no anomalous spectral behaviour to at least  $10 \times 10^9$  Pa. Unfortunately, because of extensive phonon shielding in the semiconducting materials where  $x = 1.0$  to 0.8 combined with the limitations on sensitivity with the experimental arrangement, it proved impossible to obtain data for these compositions. For brevity, we will only display and discuss the behaviour of  $\text{LaNi}_{0.5}\text{Fe}_{0.5}\text{O}_3$  although these observations will be general to the lanthanum nickel ferrates where  $x$  ranges from about 0.4 to 0.7. Some infrared spectra in the  $760\text{--}450\text{ cm}^{-1}$  spectral region of lanthanum nickel ferrate ( $\text{LaNi}_{0.5}\text{Fe}_{0.5}\text{O}_3$ ) in the pressure range  $0\text{--}3.4 \times 10^9$  Pa are shown in figure 1: at ambient pressure ( $\sim 0.1 \times 10^6$  Pa) peaks at  $620\text{ cm}^{-1}$  and around  $480\text{ cm}^{-1}$  are evident. Spectral changes in the  $620\text{ cm}^{-1}$  peak begin about  $1.2 \times 10^9$  Pa, although the  $\sim 480\text{ cm}^{-1}$  peak appears insensitive. Around  $1.4 \times 10^9$  Pa there is a dramatic change in the infrared spectrum: the—relatively—most intense peak ( $620\text{ cm}^{-1}$ ) is still apparent but there is a relatively narrow peak at about  $720\text{ cm}^{-1}$  and a relatively broad family of peaks in the spectral interval  $585\text{--}530\text{ cm}^{-1}$ . These changes are found to be reversible.

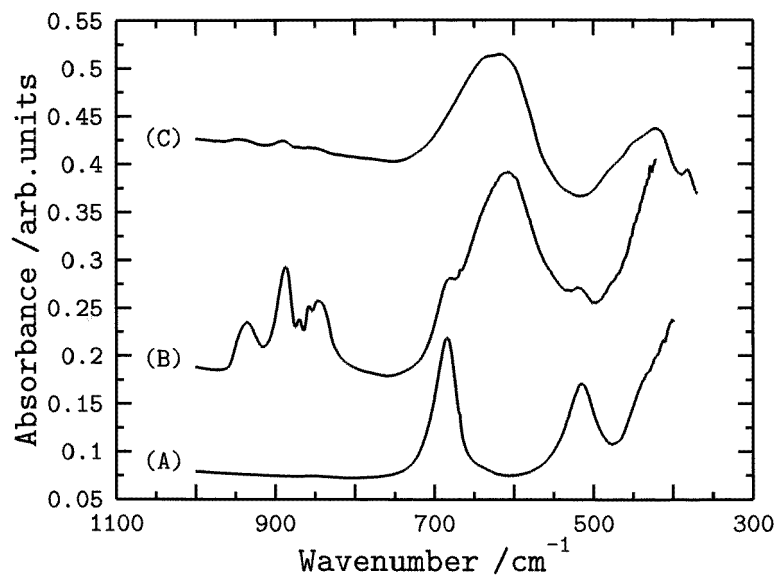


**Figure 1.** Pressure-dependent IR behaviour of  $\text{LaNi}_{0.5}\text{Fe}_{0.5}\text{O}_3$  in the  $\nu_{\text{TM-O}}$  spectral region: (A) 0, (B) 1.2, (C) 1.4 and (D)  $3.4 \times 10^9$  Pa.

These spectra are to be compared to those of  $\text{LaNi}_{0.1}\text{Fe}_{0.9}\text{O}_3$  (figure 2). In the latter spectra, there is a single peak centred around  $580\text{ cm}^{-1}$  whose wavenumber increases linearly with applied pressure to at least  $11.4 \times 10^9$  Pa. There is no evidence for splitting of the  $580\text{ cm}^{-1}$  band for this material. For all materials, bands also appear near to the low-wavenumber cut-off: they appear to be pressure insensitive. Before we can offer an interpretation of these data, it will prove useful to consider the infrared spectra and powder x-ray data of some other lanthanum transition metallates and it is to these data which we now turn.

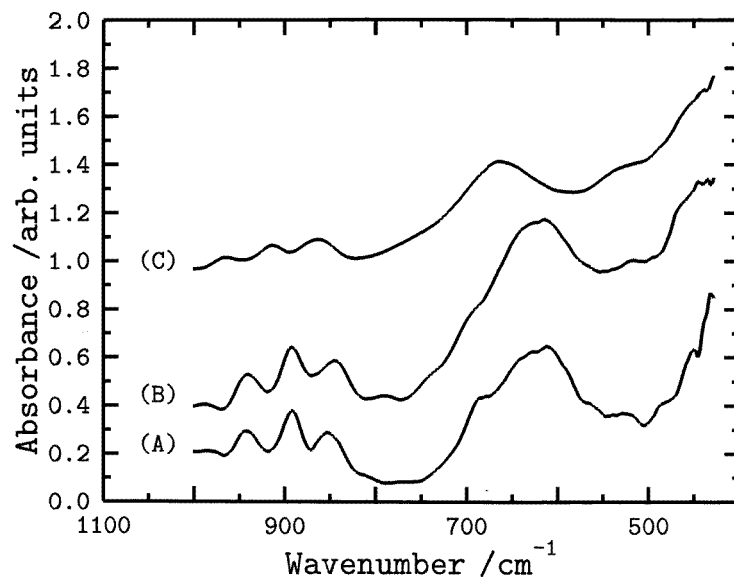


**Figure 2.** Pressure-dependent IR behaviour of  $\text{LaNi}_{0.1}\text{Fe}_{0.9}\text{O}_3$  in the  $\nu_{\text{TM-O}}$  spectral region: (A) 0.4, (B) 2.1, (C) 6.7 and (D)  $11.5 \times 10^9$  Pa.

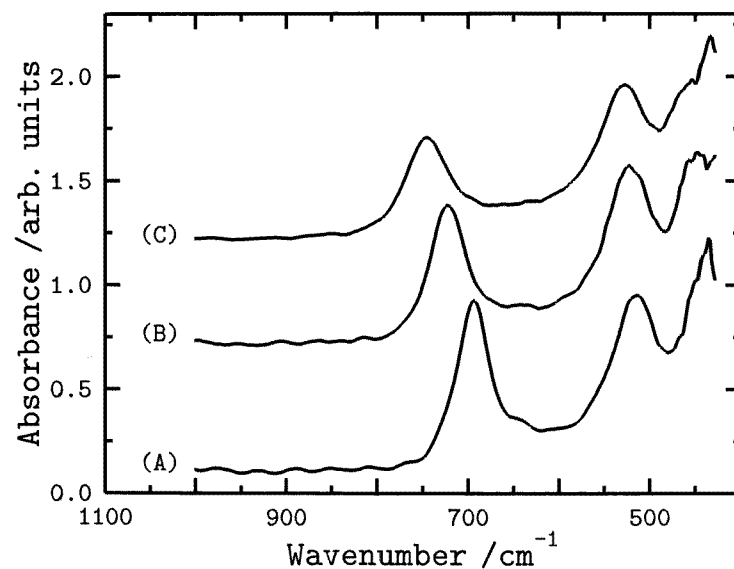


**Figure 3.** Infrared spectra of  $\text{La}_2\text{CuO}_4$  (A),  $\text{La}_2\text{Cr}_{0.5}\text{Cu}_{0.5}\text{O}_4$  (B) and  $\text{LaCrO}_3$  (C) under ambient conditions (295 K and  $0.1 \times 10^6$  Pa).

The infrared spectra of  $\text{La}_2\text{CuO}_4$ ,  $\text{La}_2\text{Cr}_{0.5}\text{Cu}_{0.5}\text{O}_4$  and  $\text{LaCrO}_3$  are shown in figure 3(A), (B) and (C), respectively (the spectra of  $\text{La}_2\text{CuO}_4$  and  $\text{La}_2\text{Cr}_{0.5}\text{Cu}_{0.5}\text{O}_4$  are normalized so that their intensities may be compared directly). The spectrum of  $\text{La}_2\text{CuO}_4$  is peculiar in that

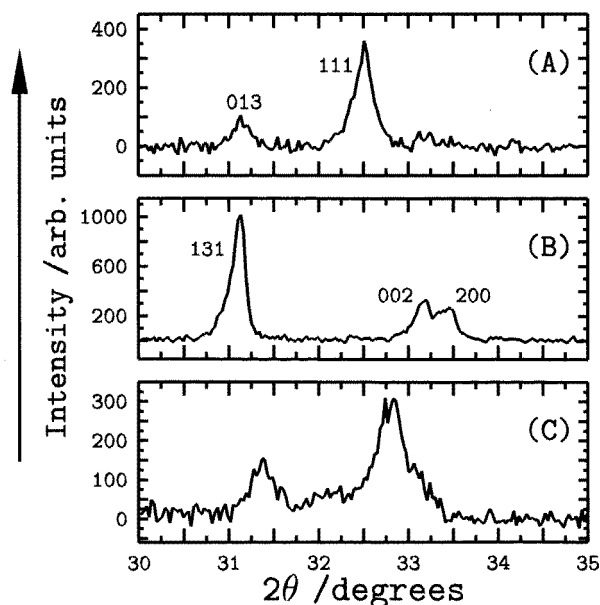


**Figure 4.** Pressure-dependent IR spectra in the  $\nu_{\text{TM-O}}$  spectral region of  $\text{La}_2\text{Cr}_{0.5}\text{Cu}_{0.5}\text{O}_4$  at 0 (A),  $0.9 \times 10^9$  (B) and  $7.0 \times 10^9$  Pa (C).



**Figure 5.** Pressure-dependent IR spectra in the  $\nu_{\text{TM-O}}$  spectral region of  $\text{La}_2\text{CuO}_4$  at 0.3 (A),  $2.7 \times 10^9$  (B) and  $5.3 \times 10^9$  Pa (C).

it exhibits two relatively narrow bands at 685 and 515  $\text{cm}^{-1}$ . In contrast, the spectrum of  $\text{La}_2\text{Cr}_{0.5}\text{Cu}_{0.5}\text{O}_4$  comprises a relatively strong broad band at 618  $\text{cm}^{-1}$  and weak shoulders at about 682 and 518  $\text{cm}^{-1}$ . The spectrum of  $\text{LaCrO}_3$  is similar to  $\text{La}_2\text{Cr}_{0.5}\text{Cu}_{0.5}\text{O}_4$  except that in the former the two weak shoulders are absent and the central peak is slightly higher



**Figure 6.** X-ray diffraction data in the  $2\theta$  range  $30\text{--}35^\circ$  for  $\text{La}_2\text{NiO}_4$  (A),  $\text{La}_2\text{CuO}_4$  (B) and  $\text{La}_2\text{Cr}_{0.5}\text{Cu}_{0.5}\text{O}_4$  (C).

in wavenumber ( $628\text{ cm}^{-1}$  compared to  $618\text{ cm}^{-1}$ ) than in the latter. We note a family of weak–medium bands around  $900\text{ cm}^{-1}$  present in  $\text{La}_2\text{Cr}_{0.5}\text{Cu}_{0.5}\text{O}_4$  are also found in  $\text{LaCrO}_3$  but with considerably less intensity.

The pressure dependencies of  $\text{La}_2\text{Cr}_{0.5}\text{Cu}_{0.5}\text{O}_4$  and  $\text{La}_2\text{CuO}_4$  are shown in figures 4 and 5, respectively. The spectrum of  $\text{La}_2\text{Cr}_{0.5}\text{Cu}_{0.5}\text{O}_4$  comprises a single relatively broad band at least up to  $7.1 \times 10^9\text{ Pa}$ . The pressure dependencies of the two bands in  $\text{La}_2\text{CuO}_4$  are somewhat different. The higher-frequency band ( $685\text{ cm}^{-1}$ ) increases with increasing pressure whilst the lower-frequency band ( $515\text{ cm}^{-1}$ ) appears relatively pressure insensitive. The two bands, however, retain their integrity up to at least  $5.3 \times 10^9\text{ Pa}$ .

X-ray powder diffraction patterns in the  $2\theta$  range  $30\text{--}35^\circ$  for  $\text{La}_2\text{NiO}_4$ ,  $\text{La}_2\text{CuO}_4$  and  $\text{La}_2\text{Cr}_{0.5}\text{Cu}_{0.5}\text{O}_4$  are shown in figure 6 (A), (B) and (C), respectively. Surprisingly, the diffraction pattern of  $\text{La}_2\text{Cr}_{0.5}\text{Cu}_{0.5}\text{O}_4$  resembles that of  $\text{La}_2\text{NiO}_4$  and not  $\text{La}_2\text{CuO}_4$ .

#### 4. Discussion

Before we offer an interpretation for the pressure-dependent spectra of, specifically,  $\text{LaNi}_{0.5}\text{Fe}_{0.5}\text{O}_3$ , we must consider a number of questions. First, for  $\text{LaNi}_{0.5}\text{Fe}_{0.5}\text{O}_3$  at ambient temperature and pressure, are both transition metal ions in the notional trivalent state or is one in the notional divalent state and the other in the tetravalent state? In either case the electron count would be the same. Second, what are the spin states of the two transition metal ions and third what assignment is to be made to the infrared spectral features which we observe?

There is little evidence to suggest significant electronic deviation from  $\text{Ni}^{3+}$  and  $\text{Fe}^{3+}$  in  $\text{LaNi}_{0.5}\text{Fe}_{0.5}\text{O}_3$  at ambient pressure. The isomer shifts for iron derived from

Mössbauer studies of  $\text{LaNi}_x\text{Fe}_{1-x}\text{O}_3$   $x = 0.05, 0.1$  and  $0.2$  [13] and  $x = 0.5$  [3] are more characteristic of  $\text{Fe}^{3+}$  than  $\text{Fe}^{4+}$ . In series such as  $\text{LaNi}_x\text{Fe}_{1-x}\text{O}_3$  [3] and  $\text{LaNi}_x\text{Cr}_{1-x}\text{O}_3$  [3] the relative vibrational intensities diminish as  $x$  tends to 1 where electron screening is more effective. However, there is little or insignificant shift of peak positions to suggest significantly differing Ni–O and Fe–O stretching forcefields and only a single broad peak around  $620\text{ cm}^{-1}$  is seen for the transition metal–oxygen stretching ( $\nu_{\text{TM-O}}$ ) modes. In transition metal ferrites [14] ( $\text{TMFe}_2\text{O}_4$ ) as well as  $\text{Fe}_3\text{O}_4$  [14] the characteristic iron–oxygen stretching  $\nu_{\text{Fe-O}}$  bands are found around  $580$  and iron–oxygen deformation modes  $\delta_{\text{Fe-O}}$  appear around  $420\text{ cm}^{-1}$ . By analogy, the spectral features in  $\text{LaNi}_{0.5}\text{Fe}_{0.5}\text{O}_3$  in the  $\sim 600\text{ cm}^{-1}$  region can be assigned to transition metal to oxygen stretching modes and those at the edge of our low-frequency window,  $\sim 450\text{ cm}^{-1}$ , to transition metal to oxygen deformation ( $\delta_{\text{TM-O}}$ ) modes, although some of the spectral activity for  $\delta_{\text{TM-O}}$  as well as the acoustic modes are beyond the wavelength cut-off of our experimental arrangement.

The pressure-induced changes of the vibrational spectrum of  $\text{LaNi}_{0.5}\text{Fe}_{0.5}\text{O}_3$  probably does not result in a mixing of the transition metal stretching and deformation coordinates since on going through and past the transition around  $1.4 \times 10^9\text{ Pa}$  the leading edge of  $\delta_{\text{TM-O}}$  within our measurement window does not show significant changes. The assignment of the  $\sim 600\text{ cm}^{-1}$  spectral region to the transition metal–oxygen stretching and the  $\sim 450\text{ cm}^{-1}$  spectral region to transition metal–oxygen deformations is therefore retained above  $1.4 \times 10^9\text{ Pa}$ .

For a number of reasons, we discount perturbations to the infrared spectra of  $\text{LaNi}_{0.5}\text{Fe}_{0.5}\text{O}_3$  arising from application of an external pressure to arise solely because of a pressure-induced high- to low-spin transition. This might be feasible for trivalent iron which is commonly found in the high-spin state but not for nickel which is expected to possess a low-spin state, as is the case [15] for instance in  $\text{LaSrFe}_x\text{Ni}_{1-x}\text{O}_4$ . Further, the manifestation of the low- to high-spin electronic phase transition in isoelectronic lanthanum cobaltate,  $\text{LaCoO}_3$ , appear quite small in the infrared: when  $\text{LaCoO}_3$  (which is predominantly high spin at ambient temperature) is subjected to increasing applied pressure and thus the  $e_g$  orbitals are depopulated because of the increasing magnitude of the crystal field splitting with increasing pressure [16], at ambient temperature, there is evidence [17] for changes of band intensity in the  $\nu_{\text{Co-O}}$  region but wavenumber shifts are either small or insignificant. Anharmonicity can also be excluded as the reason for the presence of the  $680\text{ cm}^{-1}$  pressure-induced feature since a similar phenomenon is not observed in lanthanum nickel ferrates where the ratio of nickel to iron is not approximately unity. We conclude, therefore, that in  $\text{LaNi}_{0.5}\text{Fe}_{0.5}\text{O}_3$  under zero applied pressure ( $\sim 0.1 \times 10^6\text{ Pa}$ ) both transition metal ions are in the notional trivalent state and, whatever the spin states, the  $\nu_{\text{Fe-O}}$  and  $\nu_{\text{Ni-O}}$  vibrational force fields are comparable. The mechanism of the transition requires the presence of both iron and nickel ions in approximately equal concentrations and its origins are not simply a consequence of changes in spin-state populations. We therefore ask the question, could hetero-atomic transition metal to transition metal electron transfer account for our observations? In order to assist answering this question, we consider the infrared spectra and x-ray diffraction data of some dilanthanum transition metallates.

The infrared-active bands at  $685$  and  $515\text{ cm}^{-1}$  in  $\text{La}_2\text{CuO}_4$  (figure 3(A)) have been previously assigned [18] by Singh and Ganguly to copper–oxygen stretching ( $\nu_{\text{Cu-O}}$ ) vibrations. It was commented upon that  $685\text{ cm}^{-1}$  is relatively high for  $\nu_{\text{Cu-O}}$ , but none-the-less assigned to the  $A_{2u}$  Cu–O stretch. This high-frequency band, however, was not found in the infrared spectra of praseodymium, neodymium or samarium dilanthanum cuprates. A more recent single-crystal [19] study with polarized infrared radiation allowed an unambiguous assignment of the  $685$  and  $515\text{ cm}^{-1}$  bands in  $\text{La}_2\text{CuO}_4$  to  $E_u$  and  $A_{2u}$



symmetries, respectively. Ogita *et al* [20] have noted that the  $685\text{ cm}^{-1}$  band disappears on substitution of even small amounts of La by Sr ( $\sim 3\text{ at.}\%$ ). Even though a structural phase transition, Jahn–Teller mechanism, charge density wave and anisotropic electronic shielding were considered as mechanisms for the peculiar spectral anomaly in  $\text{La}_2\text{CuO}_4$ , all of these mechanisms were excluded and the origins of the  $\sim 685\text{ cm}^{-1}$  band left unresolved.

The infrared spectrum of  $\text{La}_2\text{Cr}_{0.5}\text{Cu}_{0.5}\text{O}_4$  is very different from  $\text{La}_2\text{CuO}_4$  in that there is only a single relatively broad band centred around  $625\text{ cm}^{-1}$  with residual features at  $685$  and  $515\text{ cm}^{-1}$  which can be ascribed to  $\nu_{\text{TM-O}}$ . Since these spectra are normalized, it can be seen that the intensity of the features of  $\text{La}_2\text{CuO}_4$  are not preserved in  $\text{La}_2\text{Cr}_{0.5}\text{Cu}_{0.5}\text{O}_4$  but are considerably diminished. The electronic characteristics of chromium in the perovskite structure are those of localized electrons, and are reflected for instance in the resistivity [3] of  $\text{LaCrO}_3$  or  $\text{LaCr}_{0.5}\text{Fe}_{0.5}\text{O}_3$  ( $10^4$  and  $10^7\ \Omega\text{ cm}$ , respectively, at  $300\text{ K}$ . Fe in  $\text{LaFeO}_3$  may also be considered to be a localized system). Since perovskite-like units are retained in the  $\text{La}_2\text{CuO}_4$  structure, then it might be supposed that the chromium electrons will also be localized. The effect of—statistically—substituting every other copper ion by a chromium ion prevents the possibility of copper–copper interactions, either direct through space or through superexchange, which might otherwise give rise to charge transfer and the formation of  $\text{Cu}^{3+(+\delta q)}$  and  $\text{Cu}^{3+(-\delta q)}$  species. Such a mechanism is consistent with our x-ray powder data.  $\text{La}_2\text{CuO}_4$  belongs to the orthorhombic system *Cmca*, whereas  $\text{Pr}_2\text{CuO}_4$ ,  $\text{Nd}_2\text{CuO}_4$  and  $\text{Sm}_2\text{CuO}_4$  belong to the tetragonal system *I4/mmm*, as does  $\text{La}_2\text{NiO}_4$ . We see that the diffraction pattern of  $\text{La}_2\text{Cr}_{0.5}\text{Cu}_{0.5}\text{O}_4$  (figure 6) more closely resembles that of  $\text{La}_2\text{NiO}_4$  than  $\text{La}_2\text{CuO}_4$ , and therefore probably has the more symmetrical structure. Relatively strong anharmonicity in the  $\sim 900\text{ cm}^{-1}$  of  $\text{La}_2\text{Cr}_{0.5}\text{Cu}_{0.5}\text{O}_4$  would, however, tend to suggest that the structure is distorted to some extent, at least on the timescale of infrared spectroscopy. It is expected in general, that in series such as these where only the lanthanide ion is changing, that structural distortions arise as the lanthanide ionic radius decreases, as, for example, with the lanthanide nickelates ( $\text{LnNiO}_3$ ) or the dilanthanum nickelates ( $\text{Ln}_2\text{NiO}_4$ ) and not as the ionic radius increases. It appears, then, that other factors give rise to a structural distortion in  $\text{La}_2\text{CuO}_4$ . If the origin of the distortion is electronic in nature and that this interaction may be removed or reduced—in this case on going to  $\text{La}_2\text{Cr}_{0.5}\text{Cu}_{0.5}\text{O}_4$ —then it might be expected that a structural phase transition will occur. It is, then, unlikely that the origin of this structural change is the changes in geometrical factors on substituting copper by chromium since even a relatively small substitution of lanthanum by strontium, for example  $\text{La}_{0.925}\text{Sr}_{0.075}\text{CuO}_4$ , gives rise to the tetragonal phase (*I4/mmm*) and the  $\sim 680\text{ cm}^{-1}$  band disappears from the infrared spectrum.

The analogy between the infrared spectral behaviour of  $\text{La}_2\text{CuO}_4$  and  $\text{LaNi}_{0.5}\text{Fe}_{0.5}\text{O}_3$  now becomes evident. In the infrared spectra of  $\text{LaNi}_{0.5}\text{Fe}_{0.5}\text{O}_3$  there is a single  $\nu_{\text{TM-O}}$  band around  $620\text{ cm}^{-1}$  at ambient pressure which gives rise to spectral features higher and lower than the central band at pressures exceeding about  $1.4 \times 10^9\text{ Pa}$ . This growth of new bands arises because of increasing charge transfer from one transition metal ion type to the other as the unit-cell volume decreases, although at present it is not possible to deduce whether it is from nickel to iron or vice versa. Consequently, the force constants for  $\nu_{\text{Ni-O}}$  and  $\nu_{\text{Fe-O}}$  become sufficiently dissimilar to give rise to distinct spectral features. Conversely, charge transfer arising from copper–copper interactions and the inherent structural distortion can be reduced or removed by electronically insulating each copper ion from its copper neighbours by, in this case, substitution of one half of the copper ions by chromium ions giving  $\text{La}_2\text{Cr}_{0.5}\text{Cu}_{0.5}\text{O}_4$ . This results in readjustment of the vibrational force fields and the manifestation of new spectral features as well as the virtual removal of some others.

If, as our data for  $\text{LaNi}_{0.5}\text{Fe}_{0.5}\text{O}_3$  suggest, increasing pressure acts to favour charge

transfer, then it would be expected that the integrity of the two  $\nu_{\text{Cu-O}}$  peaks in  $\text{La}_2\text{CuO}_4$  should remain as pressure is increased: this is so (figure 5). Further, the effectiveness of electronic decoupling in  $\text{La}_2\text{Cr}_{0.5}\text{Cu}_{0.5}\text{O}_4$  can be assessed from its pressure-dependent spectral response. There is no evidence for charge transfer to at least  $7.0 \times 10^9$  Pa (figure 4).

Although we have used the term ‘charge transfer’ the Zaanen–Sawatzky–Allen [21] (ZSA) classification allows for differing types of insulator and metal-like systems. According to this classification, there are two general types of gap: the Mott–Hubbard gap due to the correlation energy  $U$  and the charge transfer gap associated with an energy  $\Delta$ . Associated with these two types of gap, there are two types of insulator: Mott insulators (where the smallest gap is associated with  $U$ ) and charge-transfer insulators (where the smallest gap is associated with  $\Delta$ ). As a result, there are two types of metal–insulator phase transition, either as the Mott–Hubbard gap closes or when the charge gap closes. It has been suggested that the latter occurs in the lanthanide nickelates [22]. We have chosen to use the term ‘charge transfer’ rather than correlation in this paper, although further work is required to establish the relative contributions of  $U$  and  $\Delta$  in these systems.

## 5. Conclusion

A pressure-induced phase transition has been located in  $\text{LaNi}_{0.5}\text{Fe}_{0.5}\text{O}_3$  at  $\sim 1.4 \times 10^9$  Pa through infrared spectroscopic techniques. The transition involves charge transfer from one type of transition metal to the other. There are probably strong electronic interactions between the copper ions in ambient-pressure  $\text{La}_2\text{CuO}_4$  giving rise to a relatively low-symmetry structure. The copper interactions can be destroyed by partial substitution of copper ions by chromium ions. On removal of the copper–copper interactions, the electronic distortions are lifted and a more symmetric structure is adopted.

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