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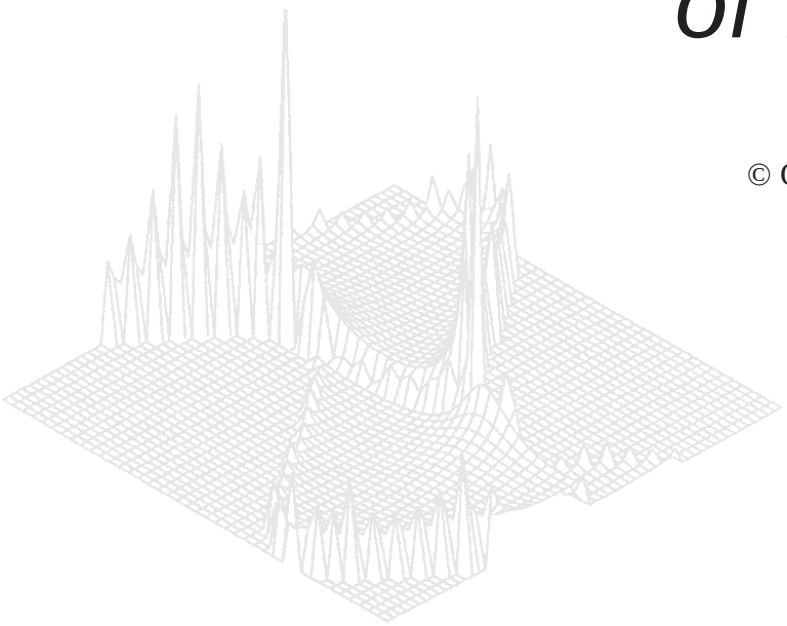

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Optical Investigation of $La_{1-x}Ca_xMnO_3$ and $La_{1-x}Li_xMnO_3$*

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Abstract

An optical study has been made of $La_{0\cdot7}Ca_{0\cdot3}MnO_3$ and $La_{0\cdot8}Li_{0\cdot2}MnO_3$ in the infrared spectral region (100 cm^{-1} to 4000 cm^{-1}). The transmission of all samples is negligible. The photoconductive response is also unmeasurable. The data reported are therefore restricted to reflectivity measurements. At room temperature, both materials exhibit similar 'bending' and 'stretching' phonon modes, associated with the MnO_6 octahedra, at ∼330 and ∼580 cm^{-1}, respectively. The 'external' phonon mode observed at ∼170 cm^{-1}, corresponding to the (La,Ca/Li) cations beating against the MnO_6 octahedra, is slightly shifted between the two materials, as would be expected on the basis of the different compositions. At elevated temperature (∼600°C) the intensity of the light reflected decreases across the infrared spectrum, and the 'stretching' mode moves to lower energy.

1. Introduction

The electrical resistivity of all materials is affected to some extent by magnetic fields, but the relative change is usually small, even at the highest fields attainable in the laboratory. The recent discovery of so-called 'colossal magneto-resistance' (CMR) in doped $LaMnO_3$ perovskites (Jin *et al.* 1994; McCormack *et al.* 1994; Urushibara *et al.* 1995) has stimulated much interest world-wide, both in the understanding of fundamental theory and the practical applications of these materials, which can exhibit a magnetic-field-induced change in electrical resistivity of orders of magnitude.

A number of experimental probes have been directed to the study of CMR materials. The fundamental phenomenon is revealed in resistivity measurements made as a function of both temperature and magnetic field. X-ray and neutron diffraction have been used to determine the nature of the crystal structure. Magnetic susceptibility, magnetisation, thermopower and heat capacity measurements all contribute to the present understanding of CMR materials. Optical spectroscopy, which is capable of giving information on lattice properties as well as on the charge carrier behaviour, is a valuable adjunct to these techniques.

The three main ways by which optical spectroscopy may be undertaken are in transmission, reflection and photoconductivity. We have attempted all three

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approaches on the CMR materials described in detail below. Both at room and at low temperature (150 K) the CMR materials show negligible optical transmission. Likewise, at room and at low temperature the CMR materials show no discernible photoconductive response, either in the constant-current or constant-voltage measurement configurations. While we will continue to investigate the possibility of transmission and photoconductivity measurements, the data reported in this paper all arise from monitoring the light reflected from the sample.

At the outset it is useful to establish the gross features of the reflectivity of CMR materials. The room-temperature spectra for all the samples examined exhibited low reflectivity in the region above 700 cm^{-1}, with the reflectivity slowly decreasing up to the highest energy employed here, 4000 cm^{-1}. Microwave measurements made at 9·3 GHz indicate that the reflectivity is essentially unity at this frequency. Thus, a transition from low to high reflectivity appears in the infrared spectral region. It is therefore in the far- and mid-infrared regions (100 cm^{-1} to 1000 cm^{-1}) that we concentrate in this paper.

Only a small number of reports deal with the optical properties of CMR materials and these have only appeared recently. Kim *et al.* (1996) discussed the infrared reflectivity of polycrystalline $La_{0\cdot7}Ca_{0\cdot3}MnO_3$, one of the materials discussed in the present paper, over the temperature range 160–300 K. They observed that the frequencies of the 'bending' and 'stretching' modes increase as the sample is cooled through the Curie temperature, T_c, from the high-temperature paramagnetic insulating state to the low-temperature ferromagnetic metallic state. They argued that a magnetoelastic effect is not the origin of the observed frequency shifts, but interpreted the shifts to mean that electron–phonon coupling (Millis 1996; Millis *et al.* 1995, 1996) as well as the double-exchange mechanism (Zener 1951; Anderson and Hasegawa 1955; de Gennes 1960) are required to explain the CMR phenomena. A material of very similar composition, $La_{0\cdot65}Ca_{0\cdot35}MnO_3$, prepared as a ∼250 nm thin film, has been examined using high resolution electron energy loss spectroscopy by Zhang and Plummer (1997), again at temperatures spanning the metal–insulator transition temperature (100, 300 and 475 K). While not strictly an optical method, this spectroscopy is also sensitive to phonon modes. The three surface phonon modes detected correspond to those in the bulk material, albeit shifted to a higher energy. The change in intensity and in energy of the phonon modes as a function of the in-plane momentum transfer is consistent with this assignment. Using a different argument Zhang and Plummer (1997) nevertheless came to the same conclusion as Kim *et al.* (1996), namely that the temperature dependence of the energy shifts points to the importance of lattice distortion coupling to the magnetic phase transition. The temperature dependence of the width and asymmetry of the phonon peaks are characteristic of a metal–insulator transition. Single crystals of a related material, $La_{1-x}Sr_xMnO_3$ ($0 \leq x \leq 0\cdot3$), have been investigated by Okimoto *et al.* (1997) using reflectivity and by Podobedov *et al.* (1998) using polarised Raman scattering. In brief, the former group concluded that an additional effect (perhaps orbital ordering or electron–lattice coupling) is required in addition to the double-exchange effect to explain the reflectivity data. The latter group observed a large shift in one phonon mode with temperature, which they attributed to a change in ionic radius, $\langle r_A \rangle$, of the La/Sr site.

2. Materials

Samples of $La_{0\cdot7}Ca_{0\cdot3}MnO_3$ were prepared either by conventional sintering or by partial melting. The former method resulted in a large number of weak-links between the grain boundaries, while the latter yielded strong-link grain boundaries; this expected morphology was confirmed by electron microscopy. X-ray diffraction indicated that both samples were polycrystalline, with no preferred orientation. The resistivity was measured at zero magnetic field and at 300 mT over the temperature range 80–290 K. The weak-link sample showed a large magneto-resistance (15–30%) over a large temperature range (90–240 K) in contrast to the strong-link sample which exhibited a smaller magnetoresistance (peak, 15%), and then only around the transition temperature (235 K). It is concluded that weak-link grain boundaries are critical in achieving a large, low-field magnetoresistance over a wide temperature range. Further details of the sample preparation and characterisation and a discussion of the importance of weak-link grain boundaries have been given by Wang *et al.* (1998*c*).

Wang *et al.* (1998*b*) found that the strong-link sample exhibits distinct steps in its magnetic susceptibility $\chi\prime$ as the temperature is varied from $4\cdot2$ K to the Curie temperature. This phenomenon has been studied as a function of the magnitude of the dc bias field and the magnitude and frequency of the ac field. Its origin is explained in terms of thermally and ac-field-activated domain wall jumps.

Samples of $La_{0\cdot8}Li_{0\cdot2}MnO_3$ were also prepared by both conventional sintering and by partial melting. Neutron powder diffraction indicates a rhombohedral perovskite structure, with the Li substituting for La. X-ray diffraction confirms the rhombohedral structure and indicates a small amount of an impurity phase in the sintered samples. The temperature dependence of the resistivity indicates a semiconductive–metallic transition in the region 200–230 K. Large magnetoresistance (up to 80%) is observed over a wide temperature range. Full details of the preparation and characterisation of this sample were given by Wang *et al.* (1998*a*).

3. Methods

For the optical measurements, the samples were polished to 1 μm. As previously described in the introduction, the CMR materials examined here exhibit negligible transmission in the infrared. Infrared photoconductivity measurements, both at room and low temperature, have likewise yielded no result. Optical measurements are therefore restricted to reflection. Near-normal incidence reflectivity was measured in the mid-infrared spectral region (500–4000 cm^{-1}) in a rapid scan Bomem interferometer using a liquid-nitrogen cooled HgCdTe detector. Measurements in the far-infrared (100–700 cm^{-1}) were made in both the Bomem and in a Polytec slow-scan interferometer using a liquid-helium cooled bolometer as detector.

4. Results and Discussion

Three samples have been examined: high- and low-density $La_{0\cdot7}Ca_{0\cdot3}MnO_3$ and low-density $La_{0\cdot8}Li_{0\cdot2}MnO_3$. Mid-infrared data are given in Fig. 1 for the low-density $La_{0\cdot7}Ca_{0\cdot3}MnO_3$ sample.

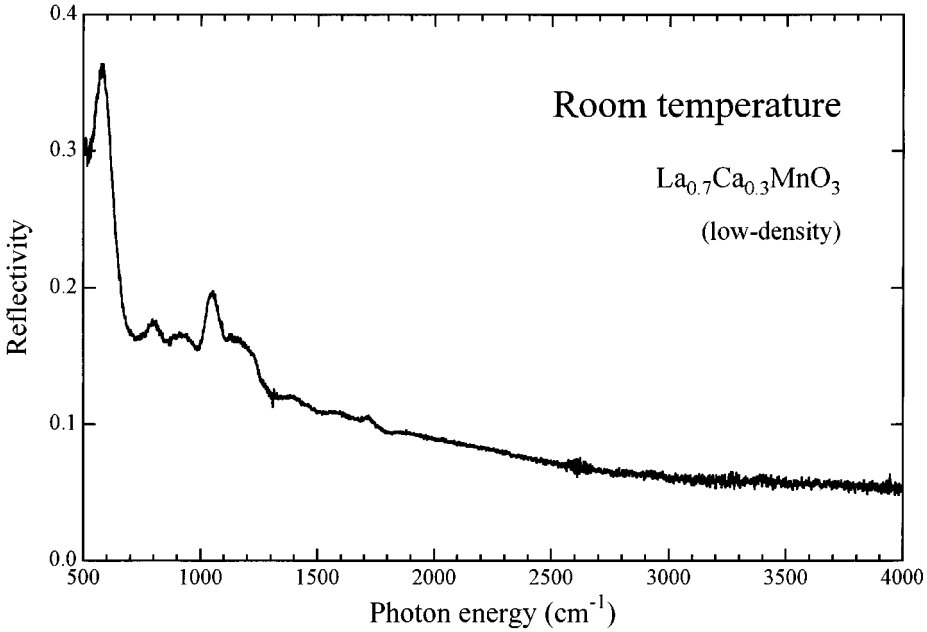

Fig. 1. Mid-infrared reflectivity of low-density $La_{0\cdot7}Ca_{0\cdot3}MnO_3$ at room temperature.

The spectrum of Fig. 1, and the room-temperature reflectivity spectra for all the samples examined, indicates low reflectivity at energies above 700 cm^{-1}, and generally decreasing reflectivity with energy to at least 4000 cm^{-1}. A similar decrease in intensity over this energy range is observed in $La_{1-x}Sr_xMnO_3$ by Raman spectroscopy (see Fig. 1 of Podobedov *et al.* 1998) and by reflectivity (see Fig. 4 of Okimoto *et al.* 1997) but has not, to our knowledge, been reported for Ca- or Li-doped manganites previously. While we have not attempted a detailed analysis of this spectrum it appears, consistent with the analysis of Okimoto *et al.* (1997) for a ferromagnetic insulator, that it would not be fitted by a conventional Drude spectrum.

Fig. 2 displays the far-infrared room-temperature reflectivity spectra of both $La_{0\cdot7}Ca_{0\cdot3}MnO_3$ and $La_{0\cdot8}Li_{0\cdot2}MnO_3$. Between 100 and 700 cm^{-1}, three distinct peaks are observed. These have been identified as optical phonon modes (Fontana *et al.* 1984; Arima and Tokura 1995; Kim *et al.* 1996). The peak near 170 cm^{-1} has been identified as an 'external' phonon mode. It derives its name from the fact that it arises from vibration of the La(Ca,Li) ions against the MnO_6 octahedra. Consistent with this interpretation, this distinctive feature shifts slightly between the $La_{0\cdot7}Ca_{0\cdot3}MnO_3$ and $La_{0\cdot8}Li_{0\cdot2}MnO_3$ samples as may be seen in Fig. 2. However, the resonance occurs at a lower frequency for the Li-doped sample than for the Ca-doped sample, whereas the lighter ion would be expected to vibrate at a higher frequency. The origin of this discrepancy requires further investigation. The peak at ∼330 cm^{-1} is identified as the Mn–O–Mn 'bending' mode. The peak at ∼580 cm^{-1} is identified as a Mn–O 'stretching' mode. As expected, since they depend essentially only on the behaviour of the MnO_6 octahedra and not directly on the identity of the cation,

the reflectivity features attributed to the 'bending' and 'stretching' modes do not differ significantly between the samples (see Fig. 2).

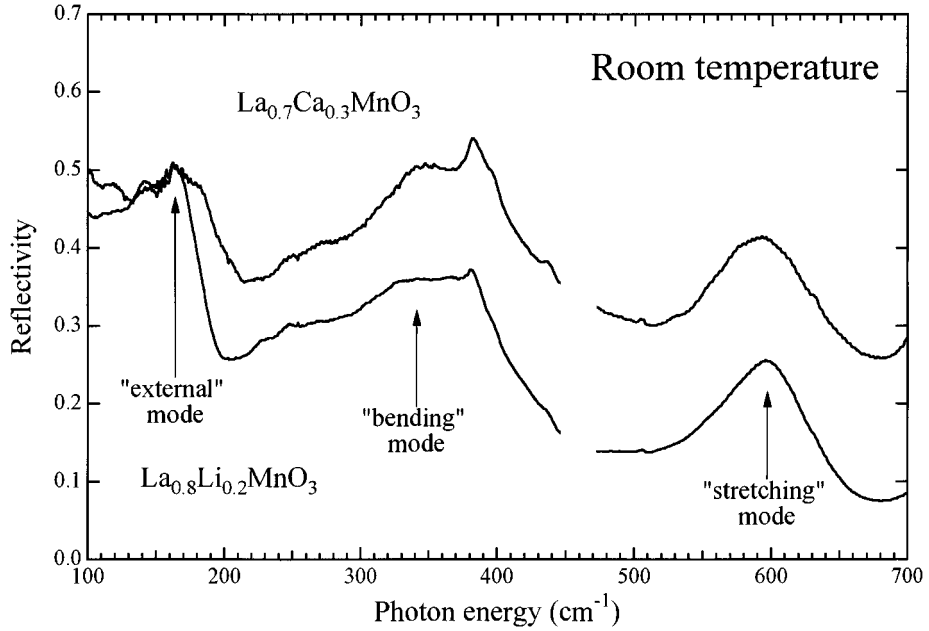

Fig. 2. Far-infrared reflectivity of $La_{0\cdot7}Ca_{0\cdot3}MnO_3$ (upper curve) and $La_{0\cdot8}Li_{0\cdot2}MnO_3$ (lower curve) at room temperature.

The reflectivity of $La_{0\cdot7}Ca_{0\cdot3}MnO_3$ and $La_{0\cdot8}Li_{0\cdot2}MnO_3$ at ~600°C is shown in Fig. 3. Three observations may be made regarding the spectra at elevated temperature. First, there appears to be an overall decrease in reflectivity, especially for $La_{0\cdot7}Ca_{0\cdot3}MnO_3$, and which is most marked around 300 cm^{-1}. The overall decrease may be in part an experimental artefact, but there nonetheless appears to be a genuine shift in spectral weight from the far-infrared; the same effect is evident in the infrared reflectivity of potassium niobate, $KNbO_3$, as reported by Fontana *et al.* (1984). Second, each of the three phonon modes discussed above decreases in intensity with temperature. Again the effect is more prominent in $La_{0\cdot7}Ca_{0\cdot3}MnO_3$ than it is in $La_{0\cdot8}Li_{0\cdot2}MnO_3$. Kim *et al.* (1996) studied the temperature dependence of the infrared reflectivity of $La_{0\cdot7}Ca_{0\cdot3}MnO_3$ and found that the intensity of the phonon modes *increased* as temperature increased in the range 160–300 K. While that observation and the present one are not necessarily incompatible, the reason for the phonon modes being most distinct at room temperature is not presently known. Third, the energies of the 'external' and 'bending' modes do not change significantly with temperature. This is consistent with the earlier investigations of Kim *et al.* (1996) and Zhang and Plummer (1997) which noted an increase in phonon energy below the Curie temperature but a constant phonon energy above it. In contrast, in the present experiments the energy of the 'stretching' mode is observed to vary as the temperature is raised. In fact, it appears that the energy decreases from the room temperature

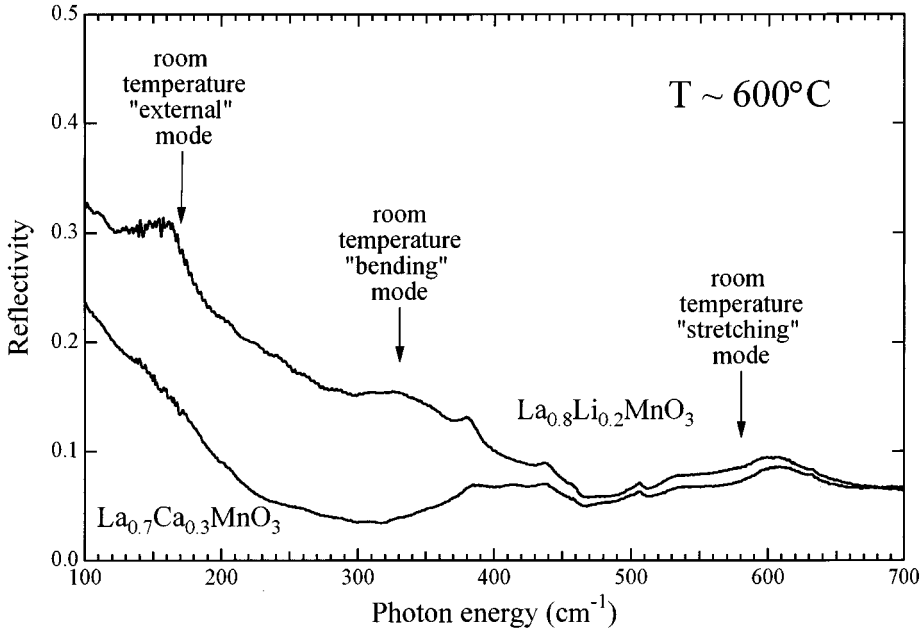

Fig. 3. Far-infrared reflectivity of $La_{0\cdot7}Ca_{0\cdot3}MnO_3$ (lower curve) and $La_{0\cdot8}Li_{0\cdot2}MnO_3$ (upper curve) at elevated temperature.

value of 580 cm^{-1} with increasing temperature as that phonon mode disappears and a new phonon mode arises at higher energy, ~620 cm^{-1} (see Fig. 3). The situation is therefore somewhat more complicated than the earlier work suggests. The full analysis of these spectra is continuing. Magneto-spectroscopy on these samples and samples of similar composition is planned.

Acknowledgments

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