Photoinduced IR absorption in \((\text{La}_{1-x}\text{Sr}_x\text{Mn})_{1-y}\text{O}_3\) : changes of the anti-Jahn-Teller polaron binding energy with doping

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Photoinduced IR absorption was measured in \((\text{La}_{1-x}\text{Sr}_x\text{Mn})_{1-y}\text{O}_3\). A midinfrared peak centered at \(\sim 5000\ \text{cm}^{-1}\) was observed in the \(x = 0\) antiferromagnetic sample. The peak diminishes and softens as hole doping is increased. The origin of the photoinduced absorption peak is attributed to the photon assisted hopping of anti-Jahn-Teller polarons formed by photoexcited charge carriers, whose binding energy decreases with increasing hole doping. The shape of the peak indicates that the polarons are small.

I. INTRODUCTION

Manganites with the chemical formula \((\text{R}_{1-x}\text{A}_x)\text{MnO}_3\) \((\text{R} \text{ and A are trivalent rare-earth and divalent alkaline-earth ions respectively})\) in which colossal magnetoresistance is observed are similar to high \(T_c\) cuprates in many ways. In both families of compounds the physical properties are strongly influenced by changing carrier concentration in relevant \(d\) and \(p\) derived electronic bands, and the interplay between lattice and electronic degrees of freedom is essential for the low energy physics of both.

It has been shown in high \(T_c\) cuprates that measurements of the photoinduced (PI) absorption are a useful tool for investigating the nature of low-lying electronic states, especially in the range of weak hole doping where PI absorption spectra are interpreted in terms of the photon-assisted hopping of small-polarons. On the other hand features in optical and Raman scattering spectra of cubic/pseudo-cubic manganites as well as related layered compounds indicate presence of small polarons. Since photoinduced transient changes of physical properties have already been observed in this class of compounds, we expect that photoinduced infrared absorption might reveal interesting spectral information about polarons also in manganites.

In this paper we present PI absorption measurements in \((\text{La}_{1-x}\text{Sr}_x\text{Mn})_{1-y}\text{O}_3\) at various hole doping, concentrating mostly on the weak hole doping levels. We find clear evidence of a photoinduced mid-infrared polaronic peak and we apply theoretical analysis to the spectra in order to deduce the dependence of the polaron binding energy on doping.

II. EXPERIMENTAL

A. Sample preparation and experimental setup

The method of preparation and characterization of ceramic samples with nominal composition \((\text{La}_{1-x}\text{Sr}_x\text{Mn})_{1-y}\text{O}_3\) \((x = 0, 0.1, 0.2)\) has been published elsewhere. Since cation deficiency is common to this class of materials, we performed AC susceptibility measurements on powders in the \(50\text{K} - 350\text{K}\) range to establish the \(\text{Mn}^{4+}\) content from their Curie temperatures. The the two Sr doped samples which we used had \(T_C \approx 210\text{K}\) and \(T_C \approx 340\text{K}\) (midpoint, see Fig. 1) for \(x = 0.1\) and \(0.2\) respectively. It was found that despite the absence of Sr the sample with \(x = 0\) showed a transition to the ferromagnetic (FM) state at \(T_C \approx 170\text{K}\). One portion of the \(x = 0\) sample was treated at \(900\text{C}\) for 300 min in Ar flow to decrease cation deficiency. This sample showed no sign of any ferromagnetic transition and so it was concluded that \(\delta\) is sufficiently small that it is antiferromagnetic (AFM) and insulating below \(T_N \approx 140\text{K}\). According to the phase diagram in Urushibara et al. the FM \(x = 0\) and \(x = 0.1\) samples are insulating below \(T_C\), while the \(x = 0.2\) sample is metallic below \(T_C\) and shows giant magnetoresistance (GMR) around \(T_C\).

Normal and photoinduced transmittance measurements in the MIR and NIR regions were performed by means of two separate Bomem MB series Fourier transform spectrometers set at 16 cm\(^{-1}\) resolution. The powder samples were mixed with KBr powder in 0.1-0.2 wt. % ratio and pressed into 12 mm diameter pellets. The pellets were mounted in the Oxford liquid-He flow optical cryostat equipped with KRS-5 windows. Special care was taken that the KBr pallet was in a good thermal contact with the sample holder.

The excitation CW Ar\(^+\)-ion-laser light with 514.5 nm wavelength \((h\nu = 2.41\text{ eV})\) was guided into the cryostat by an optical fibre. Due to space limitations in the cryostat the size of the spot illuminated by laser was only \(\sim 5\) mm...
in diameter in the center of the pellet. The maximum excitation optical fluence \( \Phi \) was \( \sim 500 \) mW/cm\(^2\). The laser excitation was switched on and off by an electro-mechanical chopper placed in the laser beam path.

To minimize heating effects due to laser light absorption in the sample and instrumental drift, the PI spectra were taken by repeating one sample scan (with excitation laser on) and one reference scan (laser off) approximately every two seconds. At each temperature the thermal-difference (TD) transmittance change was also measured without laser excitation by first measuring the reference spectrum and then increasing the sample holder temperature by 2K and measuring the sample spectrum. To remove any drifts, the same procedure was then inverted to measure the sample spectrum 2K above the given temperature first. The thermal difference (TD) transmittance change was then obtained by averaging both spectra.

B. Experimental results

The transmittance spectra \( T \) of the samples are shown in Fig. 1. First let us discuss the normal (non-photoinduced) infrared phonon spectral bands. In all FM samples we observe two IR phonon bands at 640 cm\(^{-1}\) and 400 cm\(^{-1}\). There is no appreciable shift as a function of \( x \) in the FM region of doping. In the AFM sample, the lower 400-cm\(^{-1}\) phonon band is split in two bands at 376 cm\(^{-1}\) and 420 cm\(^{-1}\) which appear further split at the peak. There are also two additional shoulders at 457 and 509 cm\(^{-1}\). The appearance of the additional phonon bands in the AF phase is in accordance with expected behaviour arising from its lower point symmetry due to the static rotation and Jahn-Teller (JT) distortion of the MnO\(_2\) octahedra compared to the FM phases\(^2\). The high frequency phonon band is shifted downwards to 585 cm\(^{-1}\) with respect to the FM samples and appears asymmetric with a shoulder like tail extending toward high frequencies. It is not clear whether this is a single phonon band or two overlapping bands.

In addition to the phonon bands we observe a broad absorption, which increases in amplitude and shifts to lower energy forming a MIR peak as the hole doping is increased in agreement with previously reported optical data\(^2\). (It should be noted that the shape of the peak in the NIR region is strongly influenced by the scattering in the KBr pellet. Fortunately, the spectral distortions due to the scattering are canceled out in PI absorption spectra.)

The low temperature \( (T = 25K) \) PI transmittance \((\Delta T/T)\) spectra of all four samples are shown in Fig. 2a. In addition, the TD transmittance \((\Delta T_{TD}/T)\) spectra taken at the same temperature are shown in Fig. 2b. In the \( x = 0 \) AFM sample a strong broad PI midinfrared (MIR) absorption (negative PI transmittance) centered at \( \sim 5000 \) cm\(^{-1}\) \((\sim 0.62 \) eV\) is observed. The virtually flat TD spectrum in Fig. 2b shows that the PI absorption is clearly not due to laser heating effects. In the frequency range of the phonon bands we observe PI phonon bleaching in the range of the 585-cm\(^{-1}\) phonon band and a slight PI absorption below 580 cm\(^{-1}\). The PI phonon bleaching consists of two peaks at 600 and 660 cm\(^{-1}\) respectively with a dip in-between at 630 cm\(^{-1}\). This two PI transmission peaks are reproducible among different runs, while the structure of the PI absorption below 580 cm\(^{-1}\) is not, and presumably arises due to increasing instrumental noise at the lower end of the spectral range.

In the \( x = 0 \) FM sample there is a much weaker PI absorption centered around \( \sim 3000 \) cm\(^{-1}\) \((0.37 \) eV\). A comparison with the TD spectrum, which shows TD transmission below 4000 cm\(^{-1}\), shows that the PI absorption is not thermally induced. The spectra in the \( x = 0.1 \) and \( x = 0.2 \) samples show no significant PI signal and are flat within the noise level. TD transmission below 2000 cm\(^{-1}\) is centered around 1200 cm\(^{-1}\) is observed in the \( x = 0.1 \) sample. The absence of any PI signal in the same sample confirms again that no thermally induced signal is present in the PI spectra, so we can eliminate thermal effects from the discussion.

To obtain information about the recombination dynamics of the PI carriers in the \( x = 0 \) AFM sample, the integrated intensity of the PI absorption peak was measured as a function of the laser fluence and is shown in Fig. 3a. It can clearly be seen that the integrated intensity of the peak is not proportional to the laser fluence \( \Phi \), but shows a square root dependence on the laser fluence \( \Delta PI \propto \sqrt{\Phi} \).

The temperature dependence of the PI-absorption-peak integrated intensity in the \( x = 0 \) AFM sample is shown in Fig. 3b. The integrated intensity quickly diminishes with increasing temperature disappearing between 80 and 100K. There is no significant shift of the PI-absorption peak observed with increasing temperature and no changes in the PI-spectra are observed around Neel temperature \( T_N \).

III. DISCUSSION

When a photon of visible light is absorbed in the sample at first the primary hole-electron pair is created. In LaMnO\(_3\) at the incoming photon energy 2.4 eV the hole-electron pair corresponds to a charge transfer from the occupied O 2p derived bands to the unoccupied Mn \( e_g \) and Mn \( t_{2g} \) derived bands\(^2,3\). The primary electron and hole are expected to relatively quickly relax by exciting secondary lower energy hole-electron pairs among other low energy
excitations (phonons, magnons), since the transport gap of 0.25 eV is almost ten times smaller than the primary pair energy.

The observed laser fluence dependence of the integrated intensity of the PI absorption peak shown in Fig. 3a indicates that the photo-excited particle density is proportional to the square root of the laser fluence. In the simplest model the photo-excited particle density \( n_{pe} \) is governed by:

\[
\frac{dn_{pe}}{dt} = \alpha \Phi - r,
\]

where \( \alpha \) is constant, \( \Phi \) laser fluence and \( r \) recombination rate. In steady state (the laser photoexcitation is pseudo-continuous in our experiment) \( n_{pe} \) is time independent and taking into account experimental fact that \( n_{pe} \propto \sqrt{\Phi} \) it follows

\[
r \propto \Phi \propto n_{pe}^2.
\]

This clearly indicates a biparticle recombination process where two independent photoexcited particles interact during recombination. The observed PI absorption peak therefore most likely corresponds to the excitations of individual electron-like and/or hole-like charge carriers created during relaxation of the primarily photoexcited electron-hole pairs.

Similar as in high \( T_c \) cuprates, in \((\text{La}_{1-x}\text{Sr}_{x}\text{Mn})_{1-y}\text{O}_y\) a PI signal of significant magnitude is observed only in the lower range of hole doping. Since the laser photoexcitation and measurement are pseudo-continuous, the photoexcited carrier lifetimes need to be quite long for any significant photoexcited carrier density to build up. Thus the absence of the PI signal at higher doping levels may not necessarily mean the absence of photoinduced carriers or polarons, but is more likely that it signifies shorter PE lifetimes. As a consequence we mainly focus on the \( x = 0 \) samples in the rest of discussion where the PI signal is observed.

In \((\text{LaMn})_{1-x}\text{O}_y\) the majority of Mn ions have one electron in the split \( e_g \) orbitals surrounded by a static JT distortion of the \( \text{MnO}_6 \) octahedra. If the photoexcitation results in an additional photoexcited hole in the occupied orbital, or an additional photoexcited electron is put into the second JT split empty \( e_g \) orbital, the Jahn-Teller mechanism is disabled and the JT lattice deformation is reduced around this site. The photoexcited charge carriers can thus form anti-JT polarons, which behave very much like ordinary polarons. One expects the characteristic shape of the PI absorption is the same as in the case of normal polarons. Indeed we find that the shape of the observed PI absorption peak is consistent with the theoretically predicted absorption due to a photon assisted hopping of small polarons as seen from the analysis that follows.

In Fig. 2a a fit of absorption due to a small polaron hopping given by \( \text{Emin}^{27} \) is shown for both \( x = 0 \) samples assuming that \( \alpha \propto -\frac{n_{pe}^2}{\Phi} \).

\[
\alpha \propto \frac{1}{\hbar \omega} \exp\left(-\frac{(2E_b - \hbar \omega)^2}{4E_b \hbar \omega_{ph}}\right)
\]

where \( \alpha \) is the absorption coefficient, \( E_b \) is the polaron binding energy, \( \omega \) the incoming photon frequency and \( \omega_{ph} \) the polaron phonon frequency. It can be seen that the theoretical prediction fits well to the data with the small polaron binding energies \( E_b = 350 \pm 8 \text{ meV} \) in the \( x = 0 \) AFM and \( E_b = 200 \pm 10 \text{ meV} \) in the \( x = 0 \) FM samples respectively. The polaron binding energies \( E_b \) and polaron phonon frequencies \( \omega_{ph} \) obtained from the fit are summarized in Table I. The obtained small polaron binding energies are similar to those inferred from transport measurement and decrease with increased hole doping in a similar manner.

The frequencies of the polaron phonons from the fit are in the region of the oxygen related modes as expected. Except for the phonon bleaching we do not observe any photoinduced local modes (PILM) in our spectra. The reason might be that the polaron phonon frequencies (indicated by Table 1) fall below the frequency range where we can reliably measure photoinduced absorption features.

Finally, it is instructive to compare the PI absorption spectrum with IR conductivity spectra of chemically doped compounds to see whether the PI carriers show any similarity to the carriers introduced by chemical means. Indeed, Okimoto et al. observe in the \( x = 0.1 \text{La}_{1-x}\text{Sr}_{x}\text{MnO}_3 \) a broad absorption peaked around 0.5 eV which is absent at room temperature and increases in intensity with decreasing temperature. Consistent with our present interpretation they attribute it to localization of JT polarons at low temperatures and relate the peak energy of 0.5 eV to a JT polaron binding energy \( E_{pJT} \). In addition, the reported absorption feature also shifts to lower energy as doping is increased in agreement with our photoinduced measurements.\(^{27}\) Midgap state with a similar peak energy and similar doping dependence was also observed by Jung et al. in \( \text{La}_{1-x}\text{Ca}_{x}\text{MnO}_3 \).

On the other hand Machida et al. and Quijada et al. report temperature dependent features in optical spectra of manganites with peak energy in the \( 1 - 1.5 \text{ eV} \) range depending on cation composition on the rare earth (R) site. The
temperature dependence of intensity and position of these peaks is consistent with small JT polaron disappearance below $T_C$. The peak energies in these experiments are much higher than $2E_b$ obtained from transport\textsuperscript{27}. Raman scattering\textsuperscript{28} and extrapolation of our data. Therefor they can not be directly related to the polaron hopping from Mn$^{3+}$ to Mn$^{4+}$ ion at energy $2E_b$ as suggested in ref\textsuperscript{29} but rather to the charge transfer between $e_g$ orbitals on neighboring Mn$^{3+}$ ions\textsuperscript{30} at energy $2E_b + U$. Here $U$ is the $e_g - e_g$ onsite Coloumb repulsion. This is additionally supported by the existence of two midgap peaks in La$_{1-x}$Ca$_x$MnO$_3$, one in the range 0.2 – 0.8 eV and another in the range 1.1 – 1.6 eV depending on $x$ attributed to the photon assisted polaron hopping from Mn$^{3+}$ to the unoccupied neighboring Mn$^{4+}$ and charge transfer from Mn$^{3+}$ the occupied neighboring Mn$^{3+}$ respectively\textsuperscript{31}.

IV. CONCLUSIONS

A photoinduced midinfrared absorption peak is observed in weakly hole doped (La$_{1-x}$Sr$_x$Mn)$_{1-d}$O$_3$ and is attributed to absorption due to photon assisted hopping of anti-JT polarons. The theoretical model for a small-polaron absorption\textsuperscript{32} fits well to the experimental data indicating that the anti-JT polarons are small with polaron binding energies of 200-350 meV, decreasing with increasing hole doping. The polaron-phonon frequencies are suggested to be in the 200-300 cm$^{-1}$ frequency range. We conclude by noting that the values of binding energies inferred from our data are in good agreement with previous transport\textsuperscript{27} and optical\textsuperscript{33} measurements, exhibiting a similar trend of decreasing with increasing hole doping.

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TABLE I. The small polaron binding energy $E_b$ and the phonon frequency $\omega_{ph}$ as obtained from the fit of absorption due to a small polaron given by Emin\textsuperscript{30}.

| sample | $E_b$ (meV) | $\omega_{ph}$ (cm\textsuperscript{-1}) |
|--------|------------|-----------------|
| (LaMn)$_{1-\delta}$O$_3$ (AFM) | $T_N \approx 140$ K | 350 ± 8 | 300 ± 40 |
| (LaMn)$_{1-\delta}$O$_3$ (FM) | $T_C \approx 170$ K | 200 ± 10 | 230 ± 76 |

VI. FIGURE CAPTIONS

Figure 1. The IR transmittance of the four samples with different Sr doping and cation deficiency. The shapes of the spectra beyond $\sim 3000$ cm$^{-1}$ are influenced by light scattering in the pellet. The inset shows the real part of the AC susceptibility as a function of temperature of the four samples. The labeling is the same as in the main panel.

Figure 2. Low temperature ($T = 25$K) a) PI transmittance and b) TD transmittance spectra as a function of doping. The spectra are vertically shifted for clarity and the thin lines represent the zero for each spectrum. Thick lines represent the small polaron absorption fit to the data.

Figure 3. The integrated PI absorption intensity in the $x = 0$ AFM sample as a function of a) the laser fluence $\Phi$ and b) temperature $T$. The solid line in the panel a) is $\sqrt{\Phi}$ fit to the data and the dashed line in the panel b) is a guide to the eye.