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Infrared optical excitations in La_2NiO_4

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Measurements are reported of the transmission of single crystals of La_2NiO_4 containing no excess oxygen. Several weak absorption bands are observed in the range 0.15–2 eV arising from magnetic and crystal-field excitations. The lowest-energy band, at 0.25 eV, is quantitatively described by a recent theory for phonon-assisted creation of a virtual bound state of two magnons. However, unlike La_2CuO_4, no higher-energy sidebands are detected, suggesting that the broad, structured absorption seen clearly in La_2CuO_4 between ~0.4 and 1 eV results from sidebands to crystal-field excitons as previously proposed.

La_2NiO_4 is an intrinsically interesting material, as evinced, for example, by the recent work of Tranquada *et al.*,[1] which reveals a rich variety of structural and magnetic phases as a function of oxygen doping. However, La_2NiO_4 with spin $S=1$, has received special attention because of its similarity to La_2CuO_4 with $S=\frac{1}{2}$, the parent material of the high-temperature superconductors $La_{2-x}Sr_xCuO_4$. It is important to identify the low-lying magnetic, electronic, and vibrational excitations of the CuO_2 layers, some of which must be involved in the superconductivity. A comparison with isostructural La_2NiO_4 can be helpful in this regard.

A controversy has recently arisen surrounding some of these low-lying excitations, which give rise to weakly electric dipole allowed infrared optical absorption bands as seen in La_2CuO_4, Nd_2CuO_4, Pr_2CuO_4, and $Sr_2CuO_2Cl_2$ by Perkins *et al.*[2] and in $YBa_2Cu_3O_6$ by Grüninger *et al.*[3] Perkins *et al.* attribute a sharp peak near 0.35 eV to a crystal-field exciton, and broad bands extending up to 1 eV to magnetic sidebands associated with this exciton. Lorenzana and Sawatzky,[4,5] on the other hand, ascribe the sharp peak to phonon-assisted creation of a quasibound bimagnon state and the sidebands to phonon-assisted multimagnon[6] excitations. To better understand these absorption bands, we have studied the optical absorption of La_2NiO_4. We observe several bands between 0.15 and 2 eV. The band at 0.25 eV is quantitatively described by the theory of Lorenzana and Sawatzky[5] for one-phonon-two-magnon absorption. However, the broad sidebands seen in La_2CuO_4 are not observed in La_2NiO_4, suggesting that the original interpretation of Perkins *et al.*[2] for the sidebands in La_2CuO_4 is correct.

The single crystal of La_2NiO_4 used in this study has been grown using the traveling-solvent floating-zone method by Hosoya *et al.* as described elsewhere.[7] The crystal is a cylinder 7 mm in diameter and several cm long with its axis along the tetragonal (110) direction. [The in-plane Ni-O bonds lie along (100) and (010).] Because of the large size of the crystal, it is possible to cut thin plates parallel and perpendicular to the c axis (001). This allows measurements with light propagating along the c axis (α polarization) or parallel to the NiO_2 layers with electric field polarized parallel (σ polarization) or perpendicular (π polarization) to the layers. Although the crystal is tetragonal at the growth temperature, upon cooling through 770 K (Ref. 8) the sample becomes orthorhombic ($Bmab$) and consequently twinned. Thus, for light propagating along the tetragonal (110) direction in σ polarization, the electric-field vector lies along the orthorhombic a and b axes with equal amplitudes.

As grown, the crystals contain excess oxygen which must be removed to make the sample transparent. Following the prescription of Hosoya *et al.*,[7] the thin plates have been annealed for 8 h at 900 °C in a mixture of 90% CO_2 and 10% CO, which establishes an oxygen partial pressure of 10^{-14} atm. To confirm that all excess oxygen is removed by this anneal, the magnetization has been measured using a superconducting quantum interference device magnetometer. The Néel temperature is found to be 335 ± 2 K, in quantitative agreement with the measurement of Hosoya *et al.*[7]

To obtain samples thin enough for transmission measurements, the plates are polished on both sides. The finished crystals are between 100 and 300 μm thick; precise measurements of thickness are used to extract absorption coefficients from the transmission data. Before measurement, the crystals are etched in 1% Br in isopropanol for 20 min to remove any surface damage or contamination from polishing. For the transmission measurements, the samples are attached to small copper blocks and placed in a helium-flow cryostat with optical windows. Two broad-band light sources, a monochromator with various gratings, and various photodetectors are used to optimize the signal in each section of the photon-energy range.

Figure 1 shows the absorption coefficient as a function of photon energy at 10 K for the three polarizations. The sharp structure below 0.15 eV corresponds to the creation of optical phonons. Above 2 eV the samples are opaque. The absorption coefficient in α polarization is larger by about 375 cm^{-1} for all photon energies above a shoulder at ~0.8 eV. Aside from this, the α and σ spectra are quite similar, revealing a peak at 0.25 eV, shown in more detail in Fig. 2, a

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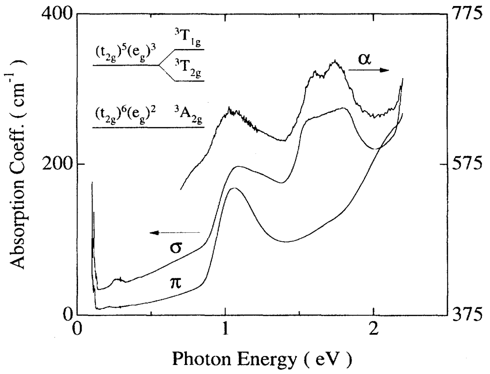

FIG. 1. Absorption coefficient versus photon energy at $T = 10$ K for two propagation directions, perpendicular (α) and parallel (σ and π) to the NiO_2 layers in La_2NiO_2. For the latter the electric field is either parallel (σ) or perpendicular (π) to the layer. The σ spectrum has been shifted upward by 20 cm^{-1}, and the α spectrum has been shifted downward as indicated by the right-hand scale. The inset shows a level diagram for Ni^{2+} in an octahedral (O_h point group) crystal field. The left part of this diagram is for noninteracting electrons (the t_{2g} levels may also be labeled by d_{xy}, d_{xz}, d_{yz}, and the e_g by $d_{x^2-y^2}$ and $d_{3z^2-r^2}$). The right part of the inset is for electron interaction strength comparable to the crystal field (Ref. 9).

peak at 1.05±0.05 eV with a shoulder on its high-energy side at ~1.25 eV, and a doublet at 1.60±0.05 and 1.75 ±0.05 eV. The peak at 1.05 eV is also present in π polarization, but the shoulder above it is missing as is the doublet at 1.6 and 1.75 eV.

Figure 2 provides a more detailed view of the low-energy portion of the spectrum. The data for σ and π are the same as for Fig. 1, but for the α spectrum a thicker sample is used for which the 0.25 eV band is more prominent relative to the background. The latter decreases with decreasing photon energy below the shoulder at ~0.8 eV. This background, which is sensitive to annealing history, gives the same attenuation for both thin and thick crystals annealed in the same way, suggesting that it arises from deviations in the oxygen stoichiometry at the surface. For each spectrum in Fig. 2, a background linear in photon energy has been subtracted. Such a background has been found to arise from surface effects in La_2CuO_4 and $Sr_2CuO_2Cl_2$.[2]

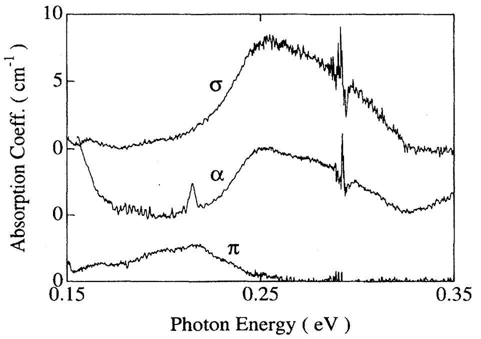

FIG. 2. Absorption coefficient at $T = 10$ K for the three combinations of propagation and polarization directions in the low-energy region. The data for σ and π are identical to those in Fig. 1, but for α a thicker crystal was used to minimize the background. The zero is shifted upward by 5 cm^{-1} for α and 10 cm^{-1} for σ.

The selection rules governing optical excitations in a uniaxial crystal are that bands appearing in α and σ but not π or only in π are electric dipole allowed, whereas bands that appear in π and α but not σ or only in σ are magnetic dipole allowed. Hence the band near 0.25 eV in α and σ and the band at 0.2 eV in π are electric dipole allowed. The component in α near 0.22 eV is so narrow that we suspect that it may be an artifact. Referring back to Fig. 1, the doublet at 1.6 and 1.75 eV and the shoulder at ~1.25 eV are also electric dipole allowed. The peak at 1.05 eV is present in all three polarizations, behavior that we discuss below.

The bands above ~1 eV are similar to those in NiO,[9] MgO containing Ni impurities, and a variety of octahedral Ni complexes.[9,10] They arise from excitations between states that result from the splitting of the Ni ion d levels by the oxygen ligands. The lowest few energy levels are sketched in the inset of Fig. 1 for octahedral coordination of the Ni ion in the high-field limit, for which the crystal-field potential is much larger than the electron-electron Coulomb interaction, and in the intermediate regime, in which these energies are comparable. The latter case is appropriate for Ni^{2+} in La_2NiO_4. Because the two excited $^3T_{2g}$ and $^3T_{1g}$ (O_h notation) states are spin triplets, transitions from the ground $^3A_{2g}$ state are spin allowed. According to Ballhausen,[9] transitions to these states are the origin of the bands in NiO at about 1 and 1.8 eV, respectively. In a tetragonal field, the spatial degeneracy of the $^3T_{1g}$ and $^3T_{2g}$ states is lifted, as seen by Iio and Nagata[11] in the spectra of K_2NiF_4 and Rb_2NiF_4, which have the same structure as the high-temperature structure of La_2NiO_4 and Ba_2NiF_6, which also has Ni ions in a tetragonally distorted octahedral coordination.

It is generally assumed that such crystal-field excitons are made weakly electric dipole allowed by coupling to optical phonons. Hence, coupling to different symmetry phonons may explain the anomalous polarization properties of the 1.05 eV peak. However, in that case it is surprising that the intensity of this band is so similar for σ and π.

The central topic of this paper is the band at ~0.25 eV. Mizuno and Koide[12] showed that a similar 0.24 eV peak in NiO results from the joint excitation of two magnons plus an optical phonon. Lorenzana and Sawatzky[4,5] have recently presented a detailed theory of this mechanism for La_2CuO_4 and La_2NiO_4. They argue that the absorption peak results from the creation of a phonon plus a virtual bound state of two magnons. This bimagnon state is relatively long lived because the magnon-magnon interaction lowers its energy enough so that the density of states for decay of the two-magnon bound state into other magnons is relatively low.

Figure 3 shows the spectrum of the 0.25 eV band together with the theory of Lorenzana and Sawatzky.[5] The two-magnon Raman-scattering spectrum of Sugai *et al.*[13] is also shown for comparison. According to Lorenzana and Sawatzky, the absorption spectrum is expected to be dominated by phonon plus two-magnon excitations with magnon pair momentum near (π,0).[14] Therefore in plotting the theoretical spectrum we take the phonon energy to be 0.066 eV,[15] which is the energy of the in-plane Ni-O stretching mode at (π,0). Further, we use the value of the antiferromagnetic exchange, $J = 0.03$ eV, found by Nakajima *et al.*[16] from neu-

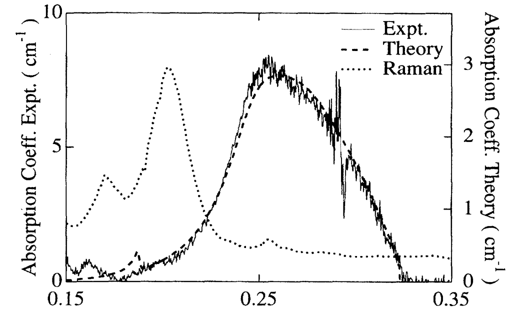

FIG. 3. Comparison between experiment (the σ spectrum from Fig. 2) and theory (Ref. 5) for the two-magnon bound state plus phonon excitation. The two-magnon Raman-scattering spectrum (Ref. 13) is also shown.

tron scattering and by Sugai *et al.*[13] from two-magnon Raman scattering. As shown in Fig. 3, the calculated absorption strength (right axis) is ~3 times smaller than that measured experimentally (left axis). It is clear that the agreement between theory and experiment is excellent, especially given that only the magnitude of the absorption has been adjusted to make the two curves coincide.

Lorenzana and Sawatzky point out that the bimagnon state is only long lived near $(\pi,0)$, where its energy is relatively low and hence there exists only a small density of free two-magnon states into which the bimagnon can decay. This makes its spectrum relatively sharp. Furthermore, a saddle point in the interacting two-magnon dispersion relation at $(\pi,0)$ yields a van Hove singularity in the bimagnon density of states. Hence, contributions from bimagnons near $(\pi,0)$ dominate the total spectrum.

It is interesting to compare the Raman and infrared-absorption spectra for two-magnon excitations (Fig. 3). The two-magnon Raman-scattering results from $k=0$ excitations, and therefore peaks at higher energy than the virtual bound state at $(\pi,0)$. Spin-wave theory predicts that the two-magnon Raman peak is at $E_R=1.71E_m$ for Heisenberg spins,[17] where E_m is the maximum one-magnon energy, in good agreement with experiment for La_2NiO_4.[13] Lorenzana and Sawatzky find that the bimagnon at $(\pi,0)$ has peak energy $\sim 1.5E_m$. However, because the optical absorption requires the creation of a phonon with energy E_p, the absorption peak is $\sim E_p-0.2E_m$ above the two-magnon Raman peak. Hence, for La_2NiO_4, where $E_m=0.124$ eV,[16] the energy difference between the Raman and absorption peaks is largely determined by the phonon energy (Fig. 3).

Figure 4 (inset) shows that the 0.25 eV peak decreases substantially in intensity and shifts to lower energy as T is increased between 110 and 300 K. This is similar to the behavior in NiO, whose peak shifts by ~0.01 eV in the same temperature range,[10] but provides an interesting contrast to La_2CuO_4 and $Sr_2CuO_2Cl_2$, whose low-energy peaks show very weak T dependence up to 400 K.[18] The zone-boundary magnon energy in the Cu oxides is nearly three times larger than that in the Ni compounds, so the bimagnons show significant T dependence at much lower temperature in the latter. Recall that the Néel transition, corresponding to three-dimensional magnetic ordering, results from the weak interlayer coupling. Hence, the similarity in the Néel temperatures for La_2NiO_4 and La_2CuO_4 does not imply similar nearest-neighbor exchange constants. A theory to explain the temperature dependence of the 0.24 eV peak in La_2NiO_4 must take the strong two-dimensional nature of the spin correlations into account. The band at 0.2 eV in π polarization may be the result of direct absorption by two magnons. For the mechanism of Tanabe *et al.*[19] this is made allowed by the lack of a center of inversion symmetry between the two Ni ions.

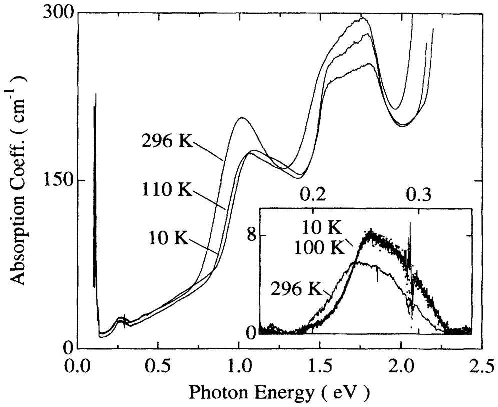

FIG. 4. Temperature dependence of the optical absorption for σ polarization. The inset shows that the 0.25 eV band shifts to lower energy with temperature between 100 and 300 K.

The theory of Lorenzana and Sawatzky is quite successful in describing the 0.25 eV band in La_2NiO_4, providing strong evidence that it results from the simultaneous creation of a phonon and a quasibound two-magnon state. This lends credence to their identification of the sharp electric-dipole allowed peak at ~0.35 eV in the layered copper oxide absorption spectra as resulting from a phonon and bimagnon as well. In the Cu oxides, the peak is sharper than that in La_2NiO_4 because the magnon-magnon interaction is stronger for spin $\frac{1}{2}$. This lowers the relative bimagnon energy into a range where the density of states for independent magnons is even lower in the copper oxide than in the nickel oxide.

For La_2CuO_4, in addition to the sharp (less than ~40 meV wide) peak corresponding to the bimagnon plus phonon absorption, Perkins *et al.*[2] observe a broad, structured absorption covering the energy range ~0.4–1.0 eV with comparable absorption coefficient but five to ten times larger width.[2,18] Lorenzana and Sawatzky suggest that phonon-multimagnon excitations can explain these sidebands. However, in our view, the absence of such sidebands in La_2NiO_4 with $S=1$, compared with their dominance in La_2CuO_4 with $S=\frac{1}{2}$, makes this explanation implausible. Specifically, any sideband absorption for La_2NiO_4 in the range 0.33–0.5 eV corresponds to less than one tenth the oscillator strength in the phonon plus bimagnon peak, whereas the strength of the extended absorption for La_2CuO_4 is at least five times larger than the sharp peak.[2,18] (The exact ratio is sensitive to manner in which the peak and continuous contributions are separated.) Thus, the relative sideband strength decreases by at least a factor of 50 between La_2CuO_4 and La_2NiO_4. Since the processes that generate multimagnon bands are related to those which generate zero-point fluctuations, they should scale similarly with S. Roughly, these should scale like $1-(M^{\dagger}/M_0)^2$, where $M^{\dagger}$ is the staggered magnetization, and M_0 is the value it would have without quantum corrections. Using the results of Igarashi,[20] one finds that $1-(M^{\dagger}/M_0)^2$ is ~ 0.6 for $S=\frac{1}{2}$ and 0.4 for $S=1$. Thus, for phonon plus multimagnon excitations, we would expect only a small decrease in the sideband strength from La_2CuO_4 to La_2NiO_4, at best a factor 2, compared with the actual value of a factor of 50 or more. This necessitates that the broad absorption in La_2CuO_4 has an alternative origin.

Perkins *et al.* suggested that the sidebands result from the creation of a $d_{x^2-y^2}$ to $d_{3z^2-r^2}$ crystal-field exciton together with one, two, three, or four magnons. They assigned the sharp peak to the bare exciton, although they recognized that it was difficult to explain how such an exciton could be made electric dipole allowed. On the other hand, the agreement between experiment and the theory of Lorenzana and Sawatzky for both La_2CuO_4 and La_2NiO_4 indicates that the sharp peak arises from phonon assisted creation of the two-magnon quasibound state. Whereas Lorenzana and Sawatzky have provided a fairly unambiguous identification of the sharp peak in La_2CuO_4, the crystal-field exciton, possibly made allowed by phonons, together with its associated magnons appears to be the only viable extant explanation of the broad, structured absorption.

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[1] J. M. Tranquada, Y. Kong, J. E. Lorenzo, D. J. Buttrey, D. E. Rice, and V. Sachan, Phys. Rev. B **50**, 6340 (1994).

[2] J. D. Perkins, J. M. Graybeal, M. A. Kastner, R. J. Birgeneau, J. P. Falck, and M. Greven, Phys. Rev. Lett. **71**, 1621 (1993).

[3] M. Grüninger, J. Münzel, A. Gaymann, A. Zibold, H. P. Geserich, and T. Kopp (unpublished).

[4] J. Lorenzana and G. A. Sawatzky, Phys. Rev. Lett. **74**, 1867 (1995).

[5] J. Lorenzana and G. A. Sawatzky (unpublished).

[6] We use "multimagnon" to refer to excitations involving more than two magnons.

[7] S. Hosoya, T. Omata, K. Nakajima, K. Yamada, and Y. Endoh, Physica C **202**, 188 (1992).

[8] J. Rodríguez-Carvajal, M. T. Fernández-Díaz, and J. L. Martínez, J. Phys. Condens. Matter **3**, 3215 (1991).

[9] C. J. Ballhausen, *Introduction to Ligand Field Theory* (McGraw-Hill, New York, 1962), p. 261.

[10] R. Newman and R. Chrenko, Phys. Rev. **114**, 1507 (1959).

[11] K. Iio and K. Nagata, J. Phys. Soc. Jpn. **41**, 1550 (1976).

[12] Y. Mizuno and S. Koide, Phys. Kondens. Mater. **2**, 166 (1964).

[13] S. Sugai, M. Sato, T. Kobayashi, J. Akimitsu, T. Ito, H. Takagi, S. Uchida, S. Hosoya, T. Kajitani, and T. Fukuda, Phys. Rev. B **42**, 1045 (1990).

[14] Momentum in units for the two-dimensional NiO_2 layer with the Ni-Ni bond distance $=1$.

[15] L. Pintschovius, J. M. Bassat, P. Odier, F. Gervais, G. Chevrier, W. Reichardt, and F. Gompf, Phys. Rev. B **40**, 2229 (1989).

[16] K. Nakajima, K. Yamada, S. Hosoya, T. Omata, and Y. Endoh, J. Phys. Soc. Jpn. **62**, 4438 (1993).

[17] C. M. Canali and S. M. Girvin, Phys. Rev. B **45**, 7127 (1992).

[18] J. D. Perkins *et al.* (unpublished).

[19] Y. Tanabe, T. Moriya, and S. Sugano, Phys. Rev. Lett. **15**, 1023 (1965).

[20] J. Igarashi, Phys. Rev. B **46**, 10 763 (1992).