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Infrared Absorption and Raman Scattering by Two-Magnon Processes in NiO

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Strong two-magnon (2*M*) Raman scattering has been observed from NiO along with first- and second-order phonon scattering. The shape of the 2*M* scattering peak is well described by a simple-cubic Green's function for interacting spin waves with an intersublattice exchange $J_2 = 148\ \text{cm}^{-1}$. The temperature shift of the scattering peak is identical to that of the 2000-cm^{-1} ir absorption peak described by Newman and Chrenko, but energy considerations require the absorption peak to be a phonon sideband of the 2*M* scattering peak, which is not seen in absorption.

I. INTRODUCTION

NiO has been widely investigated as a model magnetic semiconductor, and a candidate for a metal-insulator transition which has never been found. While much work has been done on its optical and electrical properties, little quantitative information has been available concerning the exchange interactions leading to its antiferromagnetic order and the resulting magnetic excitations. Furthermore, a strong, temperature-dependent absorption band is observed[1] near 2000 cm^{-1} which has variously been interpreted as the excitation of a zone-boundary magnon and a phonon $(M+P)$,[1] two zone-boundary magnons (2*M*),[1] and the simultaneous excitation of two magnons and a phonon $(2M+P)$,[2] among other suggestions.

In this paper we study the exchange interactions in NiO by observing the two-magnon (2*M*) Raman scattering in both halide-vapor-decomposition-grown crystals (called "green" NiO because of its transparency in thin sections) and also in "black" crystals containing excess oxygen, grown by the flame-fusion technique. In order to choose among the various mechanisms so far proposed to account for the ir band, we measure the temperature dependence of the Raman scattering between 1.4 and 600°K, and compare this to the ir data of Newman and Chrenko[1] above room temperature, which we supplement with low-temperature absorption data.

II. EXPERIMENT

The experiments were performed on samples of uncertain origin. However, some of the crystals were believed to have been grown by epitaxial vapor deposition on MgO, presumably by the decomposition of the halide.[3] These crystals were thin (200 μ thick) platelets oriented with (100) faces, and exhibited no detectable absorption between 3000 and 6000 cm^{-1}. The "black" crystals were cut into similar (100) slabs about 100 μ thick. All crystals were polished with a 3-μ diamond paste on a tin

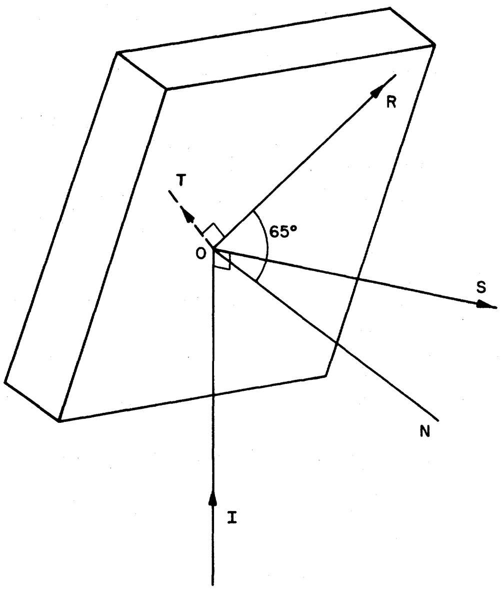

FIG. 1. Scattering geometry of a slab of single-crystal NiO containing (001) faces. The laser beam I is incident at the Brewster angle 65°. The transmitted laser beam T is normal to the reflected ray R, while the scattered radiation S is collected at right angles to I.

lap.

No attempt was made in the optical experiments to use polarized light since the crystals were in a multidomain condition, and because of the opacity of the crystal in the visible region (at the laser wavelength, 5145 Å, the absorption coefficient α for the green crystal was about 200 cm^{-1}, for the black crystal about 400 cm^{-1}). For measurements at 4.2° or below, the sample was immersed in the liquid refrigerant. At higher temperatures, the sample was in a nitrogen exchange gas, except for elevated temperatures when it was in air.

Focused argon-ion 5145-Å laser light was incident on the sample at the Brewster angle (65°) in order to minimize the reflected component, as shown in Fig. 1. Raman-scattered radiation was collected at right angles to the incident beam. This was dispersed by a Jarrell-Ash double monochromator and then detected with an S-20 photomultiplier using conventional photon-counting equipment feeding into a multichannel analyzer operating in the multiscaling mode. For typical incident optical power levels of < 100 mW from the laser, we observed signals of the order of 10^2 counts/sec at the peak of the $2M$ scattering, using a spectral bandwidth of about 9 cm^{-1}. Non-Raman contributions to the signal at the $2M$ frequency were less than 10 counts/sec. Adjacent channels of the data were uncorrelated except by noise components in the signal. In all cases the data consisted of the sum of several scans to enhance S/N.

The ir absorption measurements were carried out on a modified Beckman IR-9 spectrometer using a sample-in–sample-out technique. For measurements at low temperatures, the sample was mounted in the vacuum space of a cold-finger Dewar, equipped with NaCl windows.

III. RESULTS

A. Raman Scattering

The temperature dependence of the Raman scat-

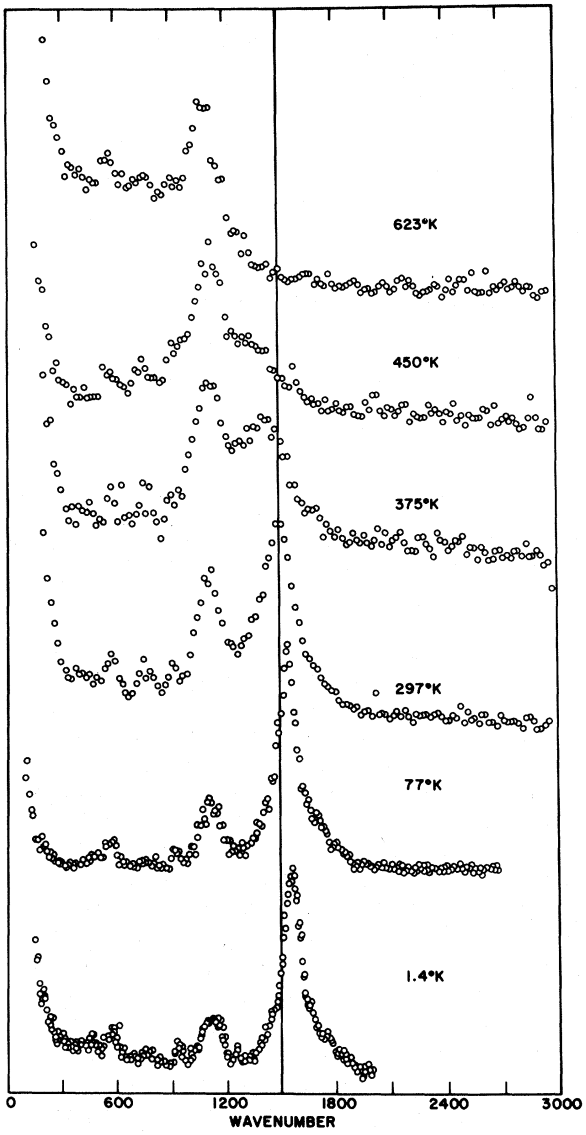

FIG. 2. Temperature dependence of Raman scattering of the 5145-Å argon line from "green" stoichiometric NiO. Above the Néel temperature (523 °K) the $2M$ scattering peak moves under the phonon lines but still appears to have considerable spectral density.

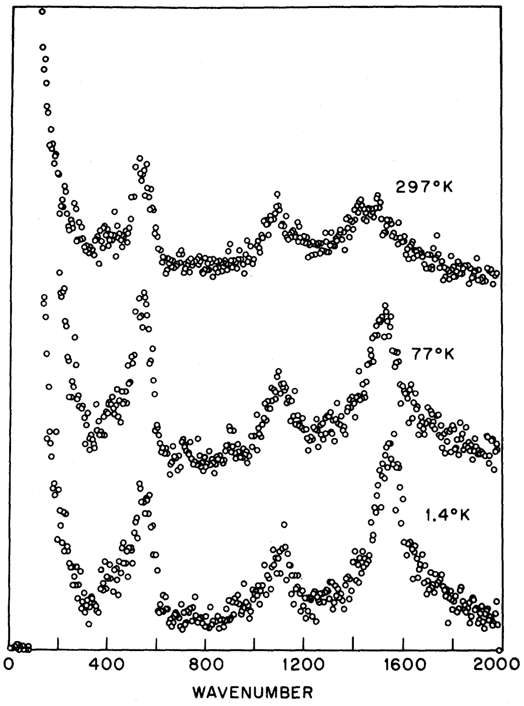

FIG. 3. Raman scattering from "black" oxygen-rich NiO. The only discernible difference between this scattering and that of Fig. 2 is the intense first-order scattering from the optical phonons between 400 and 600 cm^{-1}. The S/N is lower owing to the large absorption coefficient.

tering from green NiO using 5145-Å excitation is shown in Fig. 2, and for black NiO in Fig. 3. The ordinate scale for each temperature is arbitrary.

The scattering can be classified conveniently into a temperature-independent part (i.e., the frequency and shape do not vary) which includes all of the scattering observed between about 300 and 1200 cm^{-1} (the steeply rising edge below 300 cm^{-1} is elastically scattered laser radiation), and a temperature-dependent part, including all scattering above 1200 cm^{-1}. While we cannot determine the absolute cross section for a particular scan with any accuracy, it is clear from the data that as T increases, the temperature-dependent part becomes weaker relative to that part of the scattering which does not shift with temperature, and it is likely that the cross section of the latter part is not sensitive to temperature over a wide range (~0–600 °K).

The absolute scattering cross section is extremely large for second-order scattering. We estimate the (integrated) extinction coefficient of the $2M$ scattering at low temperatures to be 10^{-7} cm^{-1} sr^{-1} or a cross section of 10^{-30} cm^{2} sr^{-1}, including corrections for absorption, reflection, and refraction by the NiO.

The temperature-dependent part is reasonably assignable to $2M$ scattering, while the temperature-independent part must arise from phonon processes. The observed scattering peak frequencies, where "frequency" here is measured in wave-number units cm^{-1}, for the phonons are given in Table I and compared with frequencies for the TO and LO modes determined from reflectivity measurements.[4] It should be noted that the chief difference between the green and black NiO lies in a dramatic increase in the strength of the LO mode in the black NiO.

The $2M$ scattering shows the expected shift to lower frequencies, a progressive broadening with increasing T, a disappearance of a scattering peak above T_N (523 °K), where T_N is the Néel temperature, and, if we suppose that the scattering cross section of the 2LO mode is temperature independent, a decrease in the $2M$ integrated scattering cross section with increasing temperature. If the shift of the peak scattering frequency is plotted versus T on a semilog scale as in Fig. 4, we see that the shift is roughly exponential, i.e., $\Delta\omega \sim \omega_0 e^{kT/E}$, where E is determined to be 110 cm^{-1} and $\omega_0 = 4.3$ cm^{-1}. The peak scattering frequency in the black NiO (1560 ± 15 cm^{-1}) is within experimental uncertainty of the value observed for green NiO (1555 ± 10 cm^{-1}).

B. ir Absorption

We found excellent agreement between the absorption profiles of our crystals above 300 °K and the data published by Newman and Chrenko.[1] At lower temperatures, we found the peak to undergo an additional slight narrowing and shift to higher frequencies as indicated in Figs. 5 and 6. At 20 °K, the lowest temperature we investigated, the peak occurred at 2035 cm^{-1}, and had a full width at half-maximum of 360 cm^{-1}. While the absorption line does not appear quite symmetrical, the first moment of the line is determined to be 2040 ± 10 cm^{-1},

TABLE I. Observed and ir-deduced phonon scattering frequencies in wave-number units cm^{-1}.

Assigned mode		TO′	LO′	2TO	TO + LO	2LO
Predicted frequencies		400[a]	580[a]	$\gtrsim$800	$\gtrsim$980	$\gtrsim$1160
Observed:	green NiO	440[b]	560[b]	740	925	1100
	black NiO	400[b]	550[b]	···	···	1100

[a] Reference 4.

[b] Impurity-activated modes.

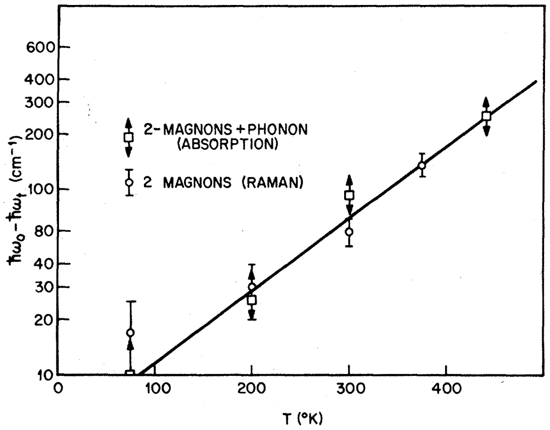

FIG. 4. Temperature shift of the peak of the Raman scattering compared to the shift of the peak of the 2000-cm^{-1} absorption band. Note the ordinate is a log scale.

with the error reflecting the uncertainty in determining the arbitrary background line. As seen in the figure, there is no trace of an absorption peak near the 2*M* Raman peak, and we conclude that the 2*M* absorption is too weak to be detected. The very weak absorption peak near 1200 cm^{-1} observed by Newman and Chrenko[1] was not strong enough to be studied in our samples.

IV. DISCUSSION

A. Raman Scattering by Magnetic Excitations

In the paramagnetic phase, NiO has the cubic NaCl structure O_h^5, each Ni ion being coordinated by a regular octahedron of oxygen ions. Efficient superexchange interactions connect each Ni to its six second neighbors along ⟨100⟩ directions, while weaker interactions connect the 12 first neighbors through the 90° paths between face-centered and cube-corner positions.

Below 523 °K, the crystal is antiferromagnetic, and the J_2 interactions now couple ions on different sublattices. On the other hand, half of the J_1 interactions couple ions on the same and half on different sublattices. While J_1 does not contribute to the Ising energy, it may make contributions to zone-boundary states. For example, Loudon and Walker[5] calculate $\hbar\omega$ at X to be $\sim 6J_2+6J_1$, while at the points Z and V it is $\sim 6J_2-2J_1$. Fortunately, J_1 is believed to be small: Preliminary values of $J_2 = 153 \pm 1.6$ cm^{-1}, $J_1^+ = -10.9 \pm 4$ cm^{-1}, and $J_1^- = -11.2 \pm 4$ cm^{-1} have been determined from inelastic neutron scattering by Samuelsen and Hutchings[6] on flame-fusion-grown NiO. A weak rhombohedral distortion of the lattice also occurs below T_N with the magnetic space group reducing to $D_{2h}(C_{2h})$. While the distortion becomes progressively larger at low temperatures, it is negligible for our purposes, since the nickel ion has an orbital singlet ground state $^3A_{2g}$, with the next-higher orbital level $^3T_{2g}$ lying some 8000 cm^{-1} higher. These states are mixed weakly with the ground state via the C_{2h} site distortion and spin-orbit coupling, and together with the dipolar interaction produce the anisotropy terms $D_1 \sim 0.64$ cm^{-1}, $D_2 \ll D_1$ responsible for the antiferromagnetic resonance,[7] and the spin orientation[8] along $[11\bar{2}]$. Since our experiments are not sensitive to the $k=0$ magnons, anisotropy is not important, contributing of the order of D_1 to the 2*M* peak frequencies, which is less than the experimental resolution.

These conditions suggest that the magnetic properties of the crystal may be well approximated by four independent simple-cubic (sc) lattices of $S=1$ spins with a single intersublattice exchange. The 2*M* excitations of the sc lattice have already been discussed by Chinn *et al.*[9] for the case of KNiF$_3$. The 2*M* excitations transform as Γ_1^+, Γ_3^+, and Γ_4^- under O_h. Chinn showed that only the Γ_3^+ states have a nonzero spectral density for a scattering

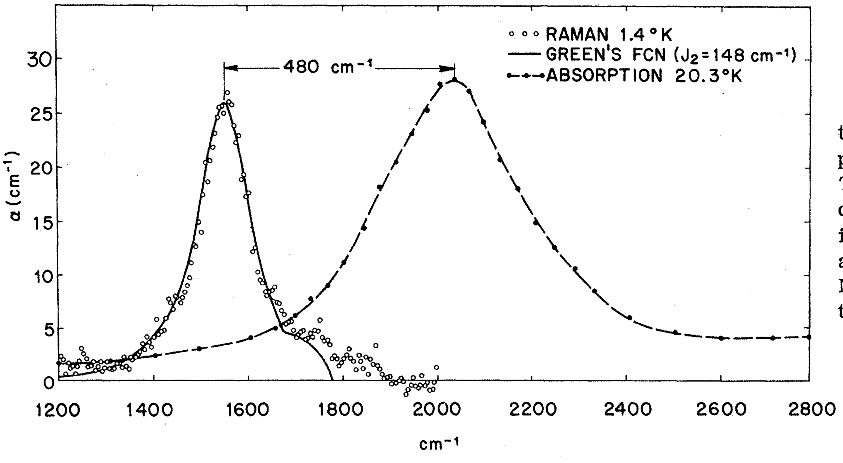

FIG. 5. Spectral shape of the low-temperature Raman scattering compared with that of the ir absorption. The solid line is a fit to the simple cubic, Γ_3^+, $S=1$, Green's function including magnon-magnon interactions, as computed by Chinn (Ref. 10). Note that the cutoff for the 2*M* scattering occurs at 1880 cm^{-1}.

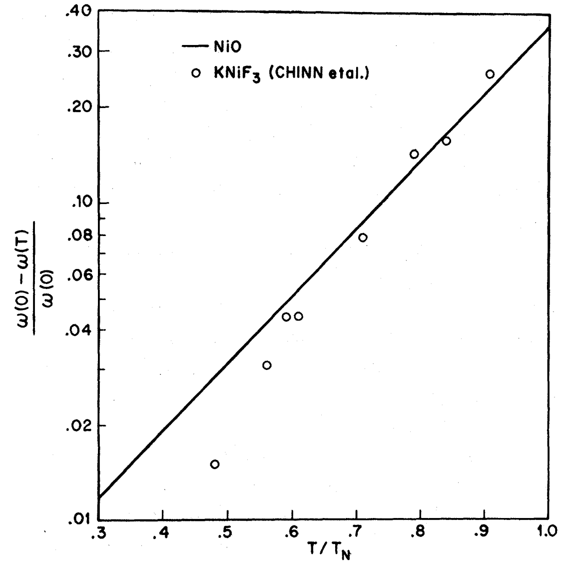

FIG. 6. Relative temperature dependence of the $2M$ scattering of NiO compared with that in $KNiF_3$, on a dimensionless plot.

matrix element of the form $\sum_{i\neq j}\mu_{ij}\vec{S}_i\cdot\vec{S}_j$ where the sum includes (in the case of NiO) second neighbors only. In Fig. 5 is plotted Chinn's Γ_3^+ Green's function,[10] scaled to a value of $J_2 = 148\ \mathrm{cm}^{-1}$. The fit to the Raman scattering at 1.4 °K is quite good except for a small shoulder on the high-frequency side of the line, which may be due to the first-neighbor exchanges. From our data, the cutoff in the $2M$ density of states is estimated at 1880 cm^{-1}, suggesting that the cutoff for the one-magnon density of state lies at $940 \pm 10\ \mathrm{cm}^{-1}$. The fit of the peak of the scattering is reliable to within two data channels or 10 cm^{-1}, or to an uncertainty in the value of the exchange integral $J_2 = 148 \pm 1\ \mathrm{cm}^{-1}$. This seems to be outside the range of values quoted for the neutron scattering ($153 \pm 1.6\ \mathrm{cm}^{-1}$) and most probably has its origin in our neglect of J_1. Since the $2M$ scattering in both green and black NiO occurred at the same frequency, we conclude that J_2 is identical for both materials within 1 cm^{-1}.

The temperature dependence of the $2M$ scattering in NiO is similar to that observed for other antiferromagnets, although the existence of a well-defined scattering peak above T_N cannot be confirmed as it was for NiF_2[11] because of interference by the phonon scattering.[12,13] The spectrum does suggest, however, that the scattering peak does not persist so strongly (in terms of the reduced temperature T/T_N) in NiO. This is to be expected since the relative importance of fluctuations should have an inverse relationship to the number of magnetic neighbors. Furthermore, the strong phonon coupling to the $2M$ states, discussed in Sec. IV D, may play an important role in decreasing the magnon-pair lifetime.

At the present time, an accurate renormalization of the $2M$ excitations is not available, and we cannot comment on the significance of the peak shift in Fig. 4, other than to remark that deviations from the apparent exponential behavior must occur at low temperature.

The value of $10^{-7}\ \mathrm{cm}^{-1}\ \mathrm{sr}^{-1}$ for the low-temperature extinction coefficient seems rather large when compared to the analogous number for NiF_2, 10^{-11}. However, it is in much better agreement with the value $\sim 3\times 10^{-8}\ \mathrm{cm}^{-1}\ \mathrm{sr}^{-1}$ determined by Chinn for $KNiF_3$ at low temperature.[10] If we assume, as in the Tanabe, Moriya, and Sugano theory,[14] that the cross section scales as the square of an off-diagonal exchange integral $|J'|^2$, and further assume that J' scales as the ground-state diagonal exchange J, and that the energy denominator is constant, we would expect to find a ratio of 10^2 instead of the observed ratio of cross sections of 10^4 for NiF_2. However, the NiO cross section is in excellent agreement with the value for $KNiF_3$, since the exchange in NiO is just a factor of 2 larger, thus scaling the expected cross section by a factor of 4. This agreement suggests that resonant contributions to the $2M$ scattering in NiO may not necessarily play a dominant role. However, this question is under further investigation.

B. Raman Scattering by Phonons

Since the $k = 0$ phonons in the paramagnetic (cubic) phase transform as Γ_4^-, no first-order scattering is expected. The observed first-order peaks near the TO (400 cm^{-1}) and LO (580 cm^{-1}) frequencies[4] must therefore derive from parity-breaking imperfections. This conclusion is confirmed by the enhancement of the first-order scattering in the black nickel oxide, where the nickel vacancy concentration is high. The remaining peaks have been assigned as combination modes. Measurements in the alkali halides[15] have shown that the combination scattering tends to vanish at the Γ point but is usually strong eleswhere in the zone. This explains why the combination peaks are all shifted down in frequency, since both LO and TO branches are expected to be depressed in frequency away from the zone center. The spectrum of NiO is unique among crystals of the NaCl structure in that the combination bands are quite narrow and all peak some 60 cm^{-1} below the Γ sum frequencies, suggesting that the dispersion of the LO and TO modes is relatively small, and that coupling between the optical and acoustic modes is relatively weak compared to the alkali halides.

The intensity of the 2LO mode may be used to scale approximately the relative intensities of the different temperature scans in Fig. 2, since the cross section of this mode is proportional (other things constant) to $(n+1)^2$, where n is the Bose factor for phonons of half the peak frequency. Thus the intensity of this peak increases from its low-temperature value by a factor of 1.2 at 300 °K to a factor of 1.8 at 600 °K. However, this procedure should be treated with considerable caution because of the known[1] variability of the absorption with temperature and frequency. As is observed for other magnetic crystals, no change in the phonon scattering is observed at the Néel temperature even though this is a first-order transition in NiO. This is to be expected since the distortion is small, and since it is magnetostrictive it increases with the magnetization. While additional phonon modes are created at $k=0$ owing to the halving of the volume of the Brillouin zone, no additional scattering is observed from these modes other than the first-order scattering we ascribe to impurities.

C. Comparison of Thermal Effects in NiO with $KNiF_3$

As we have seen, the low-temperature Raman scattering in NiO and $KNiF_3$ scales precisely with a single parameter J_2. Since this is the only significant parameter with dimensions of energy, we would expect this to be the case for any finite temperature as well. For example, the ratio of the Néel temperature to the exchange integral $T_N/J(°K) = 2.48$ for $KNiF_3$ is in excellent agreement with the value 2.44 for NiO. In Fig. 6 we plot the relative shift of the 2*M* scattering peak with the reduced temperature for both $KNiF_3$ and NiO. The agreement for the two sets of data is excellent for values of T/T_N between 0.5 and 1.0; for smaller values, the $KNiF_3$ seems to be more sensitive than the simple $e^{kT/\epsilon}$ behavior suggested by the NiO. However, both sets of data fall well within the error bars estimated for the $KNiF_3$. In addition, the greater optical density of the NiO tends to increase the possibility of local heating of the sample by the laser at low temperatures, which would have the effect of increasing the width at the nominal temperature. However, since good agreement is observed with the NiO ir shift, we expect that heating effects are not very great.

D. ir Absorption near 2000 cm^{-1}

The ir absorption near 2000 cm^{-1} has been the object of numerous speculations going back to Newman and Chrenko[1] (their paper probably contains the first allusion to any 2*M* absorption in the literature). It will be necessary to outline the characteristics of the absorption, in order to compare properly the merits of the variously proposed mechanisms.

1. *The line shape at low temperature* has little asymmetry with no wings extending far away either side of the peak frequency (at 20.3 °K, the peak frequency is 2035 ± 10 cm^{-1}). While there is a weak sample-dependent absorption underlying the peak, the process producing the peak appears to have a cutoff near 2500 ± 100 cm^{-1} on the high-frequency side, and near 1500 cm^{-1} on the low-frequency side. The full width at half-maximum (FWHM) of 360 cm^{-1} is slightly less than half the width of the base of the line.

These energies are clearly not compatible with 1*M* or 2*M* processes or with *P* processes. The magnon dispersion determined from neutron scattering[6] gives a high-frequency cutoff for the 2*M* density of states near 2000 cm^{-1}, and 2*M* absorption should coincide roughly with the 2*M* scattering peak at 1560 cm^{-1}.

The phonon frequencies can be accurately estimated from our Raman data and from ir reflectance measurements,[4] as summarized in Table I. A comparison with the lattice dynamics of isomorphic antiferromagnetic CoO ($T_N = 293$ °K)[16] strongly supports the view that the LO $k=0$ phonon is a good estimate of the highest phonon frequency in these compounds—say with 5% accuracy for CoO. Extrapolation to NiO gives a phonon cutoff at 580–620 cm^{-1} in good agreement with 610 cm^{-1} which is half of our observed high-frequency cutoff for the 2LO-mode scattering. There should be very little dispersion of the LO branch in the [001] and [111] direction, whereas in the [110] direction there are monotonic variations of phonon frequency between TO and LO.

The difference in energies between the high-frequency cutoffs for ir and Raman at 1880 and 2500 cm^{-1}, i.e., 620 cm^{-1}, corresponds accurately to the highest energy phonon estimate, whereas the peak-to-peak distance of 480 cm^{-1} (Fig. 5) agrees with an average phonon frequency [at $\vec{k}=0$, $\bar{E} = \frac{1}{3} \times (2TO + LO) \simeq 460$ cm^{-1}].

2. *The temperature dependence* strongly indicates a 2*M* origin. Newman and Chrenko observed a broadening of the ir band, rendering it unobservable above T_N. This clearly correlates ir absorption and antiferromagnetic ordering. Our extension of the data between 300 and 20 °K correlates well with these previous experiments as well as with some unpublished measurements of Torrance[17] on black NiO, enabling us to compare ir absorption and Raman scattering temperature dependence (Fig. 4). The shifts of the ir peak absorption frequency and the Raman scattering peak exhibit the same variation between 20 °K and T_N, i.e., over a range of more than $0.95 T_N$, and thus demonstrate the participation of 2*M* effects in the absorption process.

3. *The integrated intensity*, with a peak absorption coefficient $\alpha_M \sim 27$ cm^{-1} and a FWHM ~ 360 cm^{-1}, is estimated to be $\int \alpha \, d\nu \sim 10^4$ cm^{-2}, which is intermediate in strength between symmetry-allowed 2*M*

absorption ~ 10–10^3 cm^{-2} (for MnF_2,[18] where T_N and J are small and the process allowed, $\int \alpha\, dv \sim 2.5 \times 10^2\ \mathrm{cm}^{-2}$) and phonon absorption (typically 10^6 cm^{-2} with $\alpha_p \sim 10^4$). In NiO, the mechanism clearly should be quite effective and not hindered by symmetrv.

4. *Symmetry considerations*: In spite of the magnetic space group theoretic predictions of Cracknell and Joshua[19] that $2M$ absorption is an allowed transition, it is clear that this is not the case (Fig. 5). This is not surprising since the use of the full magnetic symmetry for an investigation of the $2M$ state vector (a) emphasizes the lattice distortions and spin directions which are primarily crystal-field and dipolar effects that, as previously pointed out, do not contribute importantly to the relevant matrix element, and (b) neglects completely the symmetry of the mechansim responsible for the transition. All proposed[12, 20–22] $2M$ absorption mechanisms can be expressed by an effective Hamiltonian

$$H = \sum_{\langle ij \rangle} \vec{\mathrm{E}} \cdot \vec{\pi}_{ij} (S_i^- S_i^+) \quad .$$

However, if sites i and j have a center of inversion, π_{ij} vanishes. This can be deduced for the TMS mechanism[14] from the symmetry of orbitals on sites i and j. The phonon modulated exchange of Halley also vanishes since the corresponding π_{ij} is proportional to $(\partial J_{ij}/\partial R_i) + (\partial J_{ij}/\partial R_j)$. Recent magnetostriction measurements of Bartel and Morosin[23] show that the rhombohedral distortion in NiO, below T_N, remains very small, reaching a maximum trigonal distortion angle of 4.5′ at 0 °K. The neglect of the distortion should be a very good approximation for NiO, and the $2M$ absorption is therefore strongly forbidden, in agreement with experiments.

A three-excitation mechanism ($2M + 1P$) has already been proposed by Mizuno and Koide[2] and Koide *et al.*[24] for NiO and derived from a phenomenological analysis of a Heisenberg exchange, which was postulated phonon- and radiation-dependent $J(\vec{\mathrm{E}}, \vec{\mathrm{R}})$. By expanding parameters around the equilibrium configuration, they derive an effective spin-dependent dipole moment: $(\partial^2 J/\partial \vec{\mathrm{E}}\, \partial \vec{\mathrm{R}}_k)(\vec{\mathrm{S}}_i \cdot \vec{\mathrm{S}}_j) \times \vec{\mathrm{R}}_k$. This can be expressed in terms of $2M$ and $1P$ operators and will give rise to an addition band at $E_M + E_{M'} + E_P$ and a difference band at $E_M + E_{M'} - E_P$. There is no experimental evidence for the presence of a difference band; in fact if the intensities of the two bands are related by Boltzmann factors $e^{E_P/kT}$ (although this crude picture might not agree with the details of the microscopic mechanism), the breadth of the transition would not produce a resolvable difference-band peak.

One notes with interest that Mizuno and Koide made their proposal with very little knowldege of the properties of NiO (their T_N is wrong by 120 °K, they guess the LO at 440 instead of 580 cm^{-1}, and they did not know the exchange constants) and prior to the observation of $2M$ absorption in FeF_2 and MnF_2[18, 25] and to the proposals for various $2M$ mechanisms. While the details of their theory, and those of the augmented version of Ref. 24 as well, are in poor agreement with experiment if one uses correct values for $\hbar\omega$ phonon and J, we believe their assignment of the absorption as due to a $2M+P$ excitation by a phenomenological spin-dependent dipole moment is correct.

We also note that a similar absorption band has been observed by Tsuchida[26] in KNiF_3, and interpreted using the theory of Ref. 24. In addition, some attempt was made to rationalize the identification of the phonon mode involved according to its efficiency in modulating the superexchange interaction. The T_{1u} Ni-F stretching mode was found to be most efficient and gave good agreement with the observed $2M+P$ peak frequency, using a reasonable value for J. Tsuchida also claimed good agreement for the temperature dependence of the peak frequency using the molecular field renormalization of Ref. 24. Unfortunately, the results of Tsuchida's calculations do not agree with those of Ref. 24, and Tsuchida does not give any details of his calculation. Since the molecular field model describes the temperature renormalization of pair excitations rather poorly (for example, it predicts zero linewidth at 0 °K), we will ignore it in our discussion.

It is very difficult and venturesome to give selection rules for the Mizuno-Koide mechanism since the term $\partial^2 J/\partial \vec{\mathrm{E}}\, \partial \vec{\mathrm{R}}$ depends on microscopic details. The presence in the final state of one phonon of momentum $\vec{\mathrm{k}}_p$ and of magnons of momentum $\vec{\mathrm{k}}_M$ and $\vec{\mathrm{k}}_{M'}$, such that $\vec{\mathrm{k}}_P + \vec{\mathrm{k}}_M + \vec{\mathrm{k}}_{M'} = 0$, allows a wide combination of choices. If one uses the magnetic space group symmetry of Cracknell and Joshua, one finds that the combination of any $\vec{\mathrm{k}} = 0$ phonon with $2M$ states at Γ, M, X, Z, L, V points in the magnetic Brillouin zone (B.z.) gives an electric dipole allowed transition. Further it is possible to combine three excitations at the Brillouin zone boundaries. Also, as discussed above, the phonon B.z. is twice as big as the magnon B.z. For example, $\Gamma X_{\mathrm{mag}} = \frac{1}{2}\Gamma L_{\mathrm{paramag\,(direction\,\langle 111\rangle)}}$ but $\Gamma L_{\mathrm{mag}} = \Gamma L_{\mathrm{paramag(direction\langle 11\bar{1}\rangle)}}$ which will generate additional zone-center phonon modes. Details are given by Cracknell and Joshua.[19]

In the absence of obvious selection rules, the line shape will be given by contributions from critical points in the densities of phonon and magnon states, i.e., mainly $\vec{\mathrm{k}} = 0$ and zone boundaries $\vec{\mathrm{k}}$. Further, since the effect of the phonon is to lift the selection rule for $2M$ absorption, one expects that the most efficient phonons will be optical in which the O^{2-} midway between two Ni^{2+} will vibrate out of phase with the two Ni^{2+}. One cannot say however whether TO or LO phonons are more efficient, or if coupling to the additional zone-center phonon modes below T_N is important. Neither can we say if magnon pairs of nonzero $\vec{k}$ contribute importantly; their spectral density will look quite different from the Raman scattering, and further speculation on the line shape is futile.

V. CONCLUSIONS

The optical properties of NiO are dominated by the strong exchange interactions and covalency of that material. The magnetic excitations are, nevertheless, simple, in that they are well described by spin-wave theory, with a single, dominant intersublattice exchange interaction, $J_2 = 148\ \text{cm}^{-1}$. The first-neighbor exchange is weak, as is also concluded from neutron scattering experiments,[6] but extends the density of states beyond the Ising energy $E(J_1, J_2) = 6J_2$ as predicted by Loudon and Walker.[5]

The off-diagonal exchange responsible for the scattering matrix element is also strong and appears to scale with the diagonal exchange with respect to the cross section measured for $KNiF_3$,[10] but not for NiF_2.[11]

First-order impurity-activated optical-phonon scattering and intrinsic second-order phonon scattering are observed to have peak frequencies simply related to phonon frequencies determined by ir reflection measurements, and suggest that the optical-phonon dispersion is small. The only difference between the scattering spectrum of the green (stoichiometric) and the black (containing an excess of oxygen) crystals is seen in the enhancement of the first-order phonon scattering in the black material.

ir absorption measurements of the 2000-cm^{-1} band first studied by Newman and Chrenko[1] were extended to low temperatures, and it was found that this band lies almost entirely above the high-frequency cutoff of the $2M$ density of states, and cannot be due to a simple $2M$ absorption process, but must involve a phonon as suggested by Mizuno and Koide.[2] The temperature shift of this band is identical to that of the $2M$ scattering and one can essentially consider it as a phonon sideband of the Raman scattering. However, because of the three-particle nature of this band, no existing theory can give its shape. Furthermore, a microscopic interpretation of the very large optical matrix element is lacking.

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