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Fine structure of near infrared optical absorption in NiO

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Abstract. The optical absorption spectrum of NiO is measured at low temperatures and energies between 7000 and 30 000 cm^{-1} . An assignment to cubic crystal field components of the $3d^8$ configuration of Ni^{2+} is proposed. The fine structure of the A band, showing two sharp lines at the lowest energies, 7811 and 7852 cm^{-1} , is explained by additional spin–orbit interaction, rhombohedral exchange striction and an orthorhombic transverse molecular field due to antiferromagnetic long-range order.

The excitonic transition into the lowest excited state of Ni^{2+} in magnetic insulators (${}^3A_{2g} \rightarrow {}^3T_{2g}$, in O_h symmetry notation) has frequently been used to show the exchange interaction of the magnetically ordered low-temperature phase, e.g., a doublet structure with peaks at 6812 and 6835 cm^{-1} observed at 1.8 K on antiferromagnetic (AF) KNiF_3 [1]. This was attributed to the exchange splitting of the Γ_3 component of the excited ${}^3T_{2g}$ state being absent from the related system $\text{KMgF}_3:\text{Ni}^{2+}$ [1]. Exchange splitting of the ${}^3A_{2g}$ ground state was first reported in the fluorescence of Ni^{2+} doped AF crystals like MnF_2 , KMnF_3 and RbMnF_3 [2, 3]. It is caused by the Ni^{2+} – Mn^{2+} exchange energy. Later on it was also revealed in absorption on a pure Ni^{2+} compound, K_2NiF_4 [4]. However, because of the degeneracy of the $M_S = +1$ and -1 levels of the ${}^3A_{2g}$ ground state in the two AF sublattices, an axial magnetic field must be applied in order to observe splitting of the 6898 cm^{-1} line.

In this paper we report on the zero-field splitting of the lowest energy exciton absorption line in NiO. In addition to exchange splittings we also consider exchange striction. It is well known that NiO undergoes a cubic-to-rhombohedral lattice distortion at temperatures $T < T_N = 523$ K [5]. Below the Néel temperature, T_N , the spins order ferromagnetically in (111) planes, which show AF stacking. The lattice compression along the AF vector, $k \parallel (111)$, is quite sizeable, $\Delta d/d = 1.3 \times 10^{-3}$ at $T = 0$ [6]. Hence, splitting of the ${}^3A_{2g}$ ground state in the trigonal crystal field [7] appears probable and might even be larger than the exchange splitting.

Optical absorption spectra due to intra- d^8 transitions of Ni^{2+} in NiO were first reported by Newman and Chrenko [8] and Austin *et al* [9]. However, owing to poor sample quality no detailed information on excitonic and vibronic fine structure of the spectrum was obtained. Our spectra were taken on epitaxially grown stoichiometric (green) single crystals of NiO with thickness $t = 0.1$ mm and orientation parallel to the cubic (001) plane. They allow, for the first time, to completely assign all absorption bands between 1 and 3 eV to the energy level scheme in the octahedral crystal field.

The unpolarized spectra were obtained with a Shimadzu UV-3100 and a CARY 14R spectrophotometer at wavelengths $200 \leq \lambda \leq 3000$ nm with resolutions 0.1 nm ($\lambda = 200$ –850 nm) and 0.5 nm ($\lambda = 850$ –3000 nm), respectively. Temperatures between 4.2 and 300 K were obtained with a He cooled closed-cycle or a cold-finger cryostat.

The absorption spectrum of NiO at 15 K is shown in figure 1b. Above about $27\,000\text{ cm}^{-1}$ the absorption constants are too strong to be measurable on our sample. Thin film samples [10] or reflection measurements [11] have to be used in this spectral range. Five broad bands with fine structures are observed below $26\,000\text{ cm}^{-1}$. They are denoted as A, B, C, D, E and F in order of increasing energy as indicated in figure 1. Ambiguities in the case of the overlapping B lines with the apparently single C line were removed by studying pressure (p) dependences of their energies, W [12]. The C line turns out to be much less sensitive to p than all of the eleven B lines, $dW(C)/dp \sim 3.5\text{ meV GPa}^{-1}$ and $dW(B)/dp \sim 10\text{ meV GPa}^{-1}$ at 10 K.

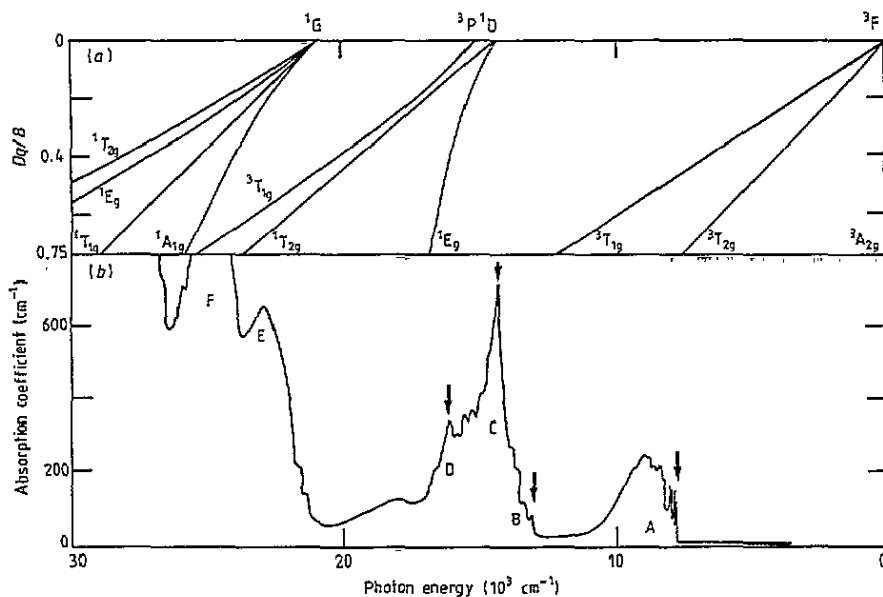


Figure 1. Energy level diagram of $\text{Ni}^{2+}(3d^8)$ in a cubic crystal field [13] with a Racah parameter $B = 1030\text{ cm}^{-1}$ (a) in comparison with the absorption spectrum of NiO at 20 K (b). The electronic origins of the A, B, C and D bands are indicated by arrows.

As temperature is increased both the A and the superimposed B + C bands grow appreciably, whereas the D and E bands and a weak band at $18\,000\text{ cm}^{-1}$ seem to be unchanged below 200 K. The integrated absorption intensities, $I(A)$ and $I(B + C)$, are plotted versus T in figure 2. Several sharp lines are observed at the low-energy side of the A band as shown for $T = 4.2\text{ K}$ in figure 3. In particular, a doublet structure denoted as A_1 and A_2 and located at 7811 and 7852 cm^{-1} respectively, is found at lowest energies. Figure 4 shows the temperature dependences of these and additional lines up to A_6 . The temperature dependences of $I(A_1)$ and $I(A_2)$ are plotted in figure 2. Peculiarly, the A_1 line grows with increasing T , whereas A_2 decreases.

The energy level diagram of Ni^{2+} in a cubic crystal field was calculated by several authors [13–16] for the $3d^8$ electron configuration. Figure 1(a) shows the ligand field energy diagram [13] using a Racah parameter $B = 1030\text{ cm}^{-1}$ and treating the cubic field parameter Dq as a variable. When choosing $Dq/B = 0.75$ the electronic origins of the bands A–E satisfactorily coincide with the transitions from the ground state ${}^3A_{2g}$ to the excited states ${}^3T_{2g}(A)$, ${}^3T_{1g}(B, C)$, ${}^1E_g(D)$ and ${}^1T_{2g}(E)$, respectively.

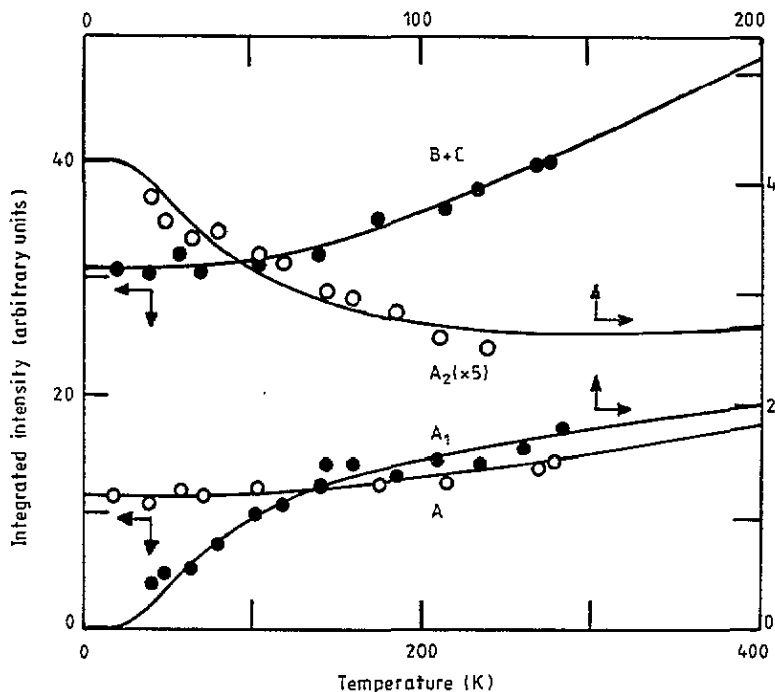


Figure 2. Temperature dependences of the integrated intensities of the A and B + C bands (figure 1) and of the A_1 and A_2 lines (figure 4), respectively. Solid curves are the best fits to theoretical expressions (see text).

All excited states except 1E_g and $^1T_{2g}$ exhibit spin-orbit splitting. For example, the $^3T_{1g}$ state, which is responsible for the B band is split into the E_g , T_{2g} , T_{1g} and A_{1g} levels. According to Germann [16], the A_{1g} , T_{1g} and E_g spin-orbit levels lie $1000\text{--}2000\text{ cm}^{-1}$ below the upper T_{2g} level. The C band is located at about 1200 cm^{-1} above the B band. Therefore the B band is attributed to the transition from $^3A_{2g}(T_{2g})$ into the $^3T_{1g}(A_{1g} + T_{1g} + E_g)$ spin-orbit levels, while the C band refers to the $^3T_{1g}(T_{2g})$ level. This assignment is consistent with the fact that the B and C bands show different pressure dependences [12].

Taking into account spin-orbit splitting [16] the other bands, A, D, E and F, can be attributed to the transitions into the levels $^3T_{2g}(A_{2g} + T_{1g} + E_g + T_{2g})$, $^1E_g(E_g)$, $^1T_{2g}(T_{2g})$ and $^3T_{1g}(A_{2g} + T_{1g} + E_g + T_{2g})$. Within this scheme the flat absorption band at approximately 18000 cm^{-1} (figure 1) remains unexplained. We propose this band to be due to a double excitonic transition [17] $^3A_{2g} + ^3A_{2g} \rightarrow ^3T_{2g} + ^3T_{2g}$, which is expected at twice the peak energy, $\sim 9000\text{ cm}^{-1}$, on the A band, $^3A_{2g} \rightarrow ^3T_{2g}$.

For the parity-forbidden, but spin-allowed bands such as A, B and C the absorption is induced by electron-lattice interaction. The temperature dependence of the intensity is given by $f(T) = f_0 + f_1 \coth(h\nu/2k_B T)$, where h and k_B are Planck's and Boltzmann's constants, respectively, and ν is the effective frequency of the lattice vibrations [18]. The solid lines in figure 2 are best fitted to the experimental data with $f_0/f_1 = 1.18$ and $\nu = 295\text{ cm}^{-1}$ for the A band and $f_0/f_1 = 0.91$ and $\nu = 293\text{ cm}^{-1}$ for the B+C bands. Since nearly identical frequencies emerge in both cases, we conclude that our assignments of the A, B and C bands are reasonable.

As mentioned above and shown in figure 5, the A band is caused by the electronic transition from the $^3A_{2g}(O_h)$ ground state into the excited $^3T_{2g}(O_h)$ state [19, 20]. Exchange

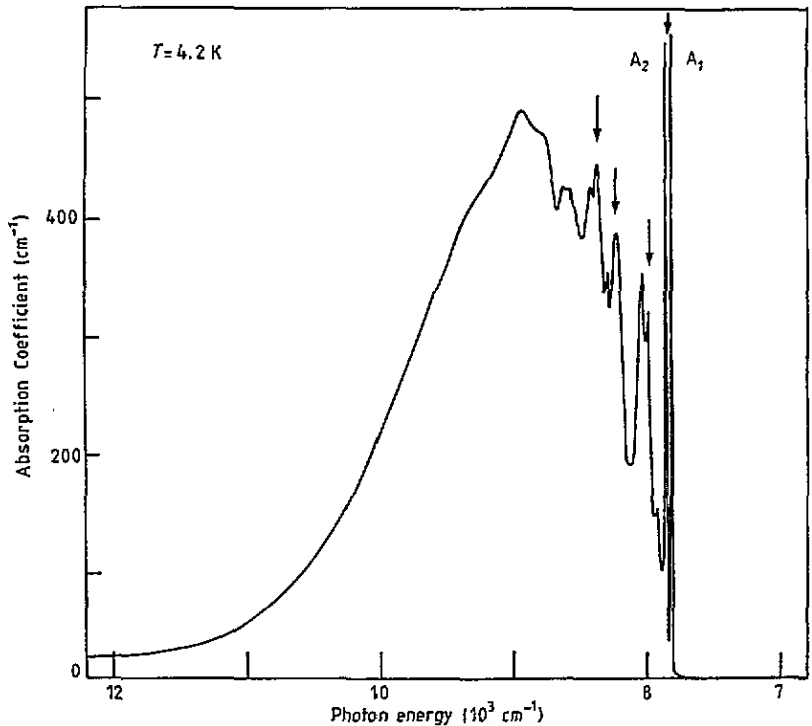


Figure 3. Fine structure of the A band measured at $T = 4.2$ K. The tentative transitions into the spin-orbit components E_g , T_{1g} , T_{2g} and A_{2g} of the excited state orbital ${}^3T_{2g}(O_h)$ are denoted by arrows.

striction causes a cubic (O_h)-to-rhombohedral (D_{3d}) lattice distortion in AF NiO at $T < T_N = 523$ K [5]. As a consequence, degenerate spin-orbit terms can be split. It is seen that the ground state ${}^3A_{2g}(O_h)$ splits into two levels, $\Gamma_1^+(D_{3d})$ and $\Gamma_3^+(D_{3d})$, whereas the first excited state ${}^3T_{2g}(O_h)$ refers to $\Gamma_3^+(D_{3d})$ [16]. Additionally, one has to account for the Ni-Ni pair interaction due to quantum-mechanical exchange. This can be treated in molecular field approximation as, for example, applied to K_2NiF_4 [4]. Since the spins in NiO are ferromagnetically aligned perpendicularly to the rhombohedral axis and parallel to cubic (111) planes, it seems reasonable to introduce a transverse molecular field component. It refers to the ferromagnetic nearest neighbour exchange constant, $J_1/k_B = 16$ K [21]. The point group symmetry is lowered to C_{2h} by this interaction. This causes all $\Gamma_3^+(D_{3d})$ levels to split into $\Gamma_1^+(C_{2h})$ and $\Gamma_2^+(C_{2h})$ (figure 5). Owing to interactions with twelve nearest neighbours, a total splitting of $\Delta E \sim 12J_1 \sim 130$ cm^{-1} is expected for the $\Gamma_3^+(D_{3d})$ level of the ${}^3A_{2g}(O_h)$ ground state. It finally consists of three levels denoted as $\Gamma_1^+(a) + \Gamma_1^+(b) + \Gamma_2^+(b)$ in C_{2h} symmetry (figure 5).

The A_1 and A_2 lines (figure 4) are attributed to the transitions from $\Gamma_1^+(b)$ and $\Gamma_1^+(a)$ into the first excited state denoted as $\Gamma_1^+(c)$ (arrows in figure 5). We calculate their intensities by using their energy difference, 41 cm^{-1} , and taking into account the thermal populations of $\Gamma_1^+(a)$ and $\Gamma_1^+(b)$ and vibration-assistance with the parameters $f_0/f_1 = 1.19$ and $\nu = 295$ cm^{-1} (figure 2). Assuming the transition probability of the A_1 line to be 4.8 times larger than that of the A_2 line, we obtain a good fit to the experimental data (solid curves in figure 2). This result lends support to our level assignment involving thermal

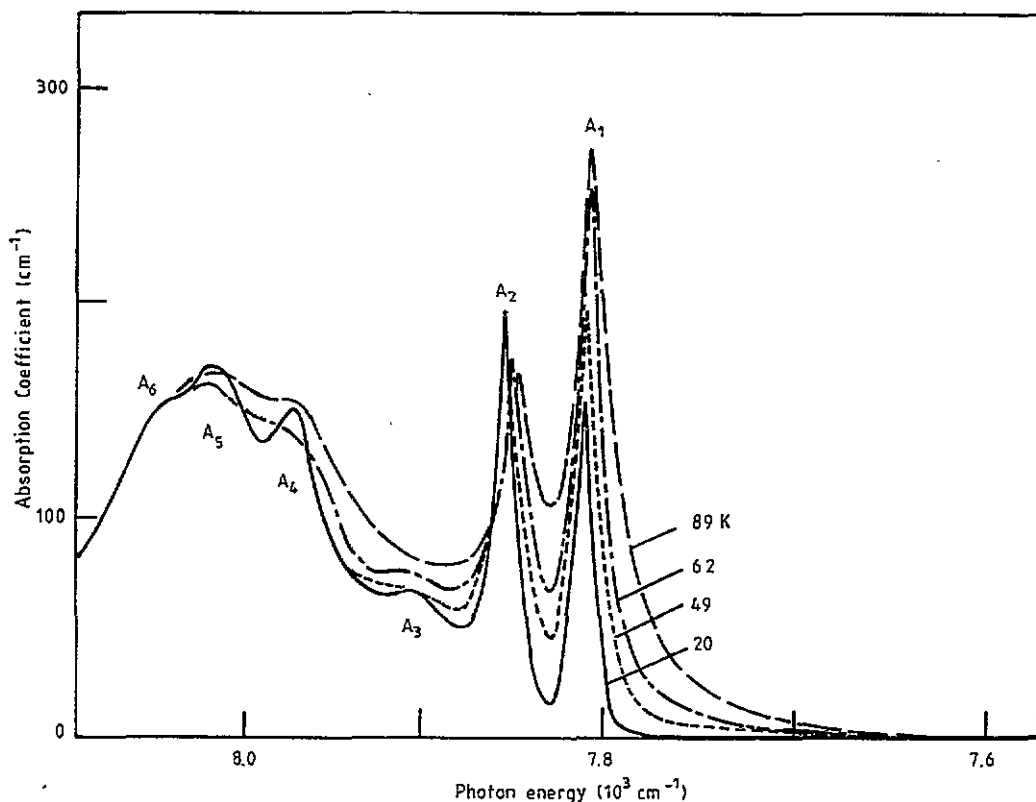


Figure 4. Absorption lines A_1 – A_6 measured at $T = 20, 49, 62$ and 89 K.

activation of the A_1 line intensity.

The AF coupling along the rhombohedral axis [5, 6] is described by an axial molecular field component. This, however, does not cause splittings of the levels assigned in figure 5. It is expected to give rise to shifts in proportion to the AF order parameter, namely the sublattice magnetization. Since this is virtually constant up to $T \sim T_N/2 \sim 260$ K, it does not affect the T dependence of the absorption lines observed in the low- T range. The $\Gamma_2^+(b)$ level of the ${}^3A_{2g}(O_h)$ ground state is virtually empty at low T because of its large distance from the lowest $\Gamma_1^+(a)$ level, $\Delta E \sim 12J_1 + 41 \text{ cm}^{-1} \sim 170 \text{ cm}^{-1}$. However, asymmetric broadening of the A_1 line towards lower energies is observed upon heating (figure 4). This seems to confirm gradual thermal population of $\Gamma_2^+(b)$ thus corroborating our energy level assignment.

Closer inspection of the low-temperature spectrum yields at least 16 distinct lines or shoulders within the A band (figure 3). The most prominent ones are denoted as A_1 – A_6 in figure 4. According to figure 5 a total number of 18 lines referring to purely electronic origins is expected when allowing for transitions from the ground state levels $\Gamma_1^+(a)$ and $\Gamma_1^+(b)$ into the different excited Γ_1^+ and Γ_2^+ levels. Accidental degeneracies and additional magnon-, phonon- and magnon-phonon sidebands make unambiguous assignments to theoretically predicted transitions difficult. Tentatively, by comparing with the energy splittings of related spectra in KNiF_3 [1] and K_2NiF_4 [4], we suggest that the peaks A_4 (7980 cm^{-1}), A_7 (8205 cm^{-1}) and A_8 (8360 cm^{-1}) (arrows in figure 3) refer to transitions

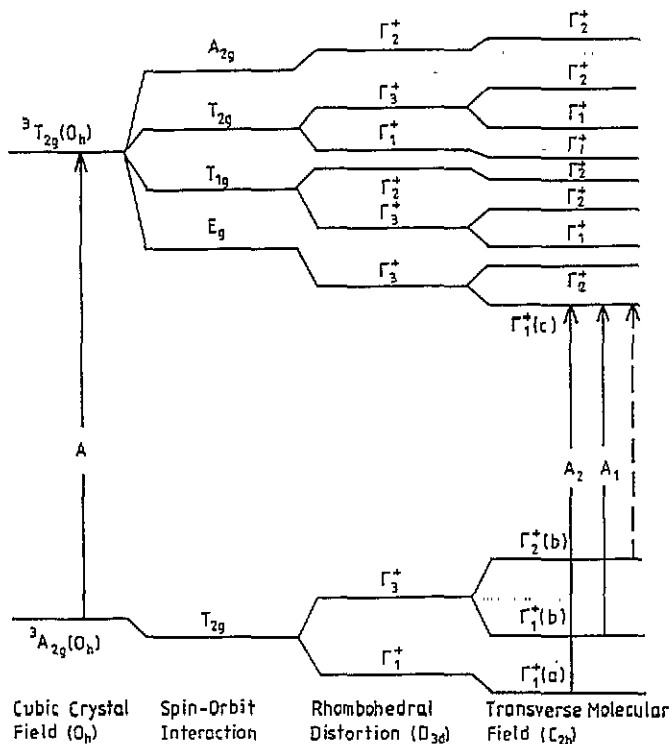


Figure 5. Schematic energy level diagram of the $3d^8$ configuration of Ni^{2+} in NiO in the A absorption region taking into account cubic and rhombohedral crystal fields, spin-orbit interaction and a transverse molecular field. The A_1 and A_2 transitions are denoted by arrows. The dashed arrow denotes the thermally activated A band precursor (figure 4).

from $\Gamma_1^+(b)$ to suitable components of the spin-orbit states T_{1g} , T_{2g} and A_{2g} of the ${}^3T_{2g}(O_h)$ excited state orbital. Nearby satellites, A_5 (8020 cm^{-1}) and A_9 (8400 cm^{-1}), probably correspond to transitions starting at $\Gamma_1^+(a)$, thus defining doublets $A_4 + A_5$ and $A_8 + A_9$ in analogy to $A_1 + A_2$.

In conclusion, doublet fine structures appear within various optical transitions from the ${}^3A_{2g}$ ground state into spin-orbit components of the first-excited-state orbital, ${}^3T_{2g}(O_h)$, of Ni^{2+} in NiO. They are most clearly revealed by the A_1 and A_2 lines at lowest energies. Their dependences on T and p [12] are compatible with a splitting of the ground state due to the rhombohedral lattice distortion and to the transverse molecular field owing to intraplanar ferromagnetic spin order. This distinguishes NiO from previously investigated Ni^{2+} compounds like KNiF_2 and K_2NiF_4 , which lack doublet line splittings in zero external field.

Acknowledgments

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