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Absorption Spectrum of Single Crystals of NiI_2 at 300–5 K

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Assignments of the electronic transitions of NiI_2 are made on the basis of single-crystal absorption spectra at temperatures down to 5 K. In addition to the ligand field transitions, from which a value of Dq = 740 cm^{-1} has been derived, an unusual absorption with a temperature-independent oscillator strength has been attributed to intervalence charge transfer. In making assignments for NiI_2 new calculations of the energy levels in all the nickel dihalides were performed using the free-atom method of Ferguson.

Introduction

The spectra of NiF_2, $NiCl_2$, and $NiBr_2$ have been the subject of numerous studies,[1] using single-crystal and diffuse-reflectance techniques, but only the mull spectrum of NiI_2 has been recorded.[2] Although many detailed spectroscopic studies of Ni(II) in chloride, bromide, and particularly fluoride lattices have been reported, investigations in iodide lattices are very rare, and, in general, the ligand field spectra of transition metal iodide complexes have received little attention. Thus, since the quality and resolution of mull spectra are not good, the single-crystal spectra of NiI_2 were clearly required, particularly since the spectrum has not been recorded at liquid helium temperatures and parameters have not been fitted to the observed absorptions. Furthermore, the single-crystal technique affords quantitative intensities, of particular interest in view of reports of anomalously intense spin-forbidden transitions in $NiCl_2$, $NiBr_2$, and various Ni(II) chloro and bromo complexes,[3-7] which have been ascribed to magnetic exchange interactions. In addition, some multiplicity-forbidden transitions in the spectra of $FeCl_2$, $FeBr_2$, $CoBr_2$, and $NiBr_2$, which are metamagnets like NiI_2, have shown[8-10] a sharp decrease in intensity below the Néel temperature T_N, a fact which has been related to the coupling of the electronic excited states with thermally excited magnons.

Crystal and Magnetic Structure

Nickel diiodide has[11] the cadmium dichloride type crystal structure, and the parameters of the pseudohexagonal unit cell are a = 3.88 and c = 19.6 Å; the structure consists of layers of cubic close-packed iodide ions with Ni^{2+} ions filling all the sites in every second layer of octahedral holes between them. These octahedral holes are trigonally distorted, so that the site symmetry of the cations is D_{3d}, but this distortion is small as indicated by the fact that the ratio of the unit-cell parameters, c/a = 5.04, is relatively close to the value 4.90 for a perfectly octahedral site. (Some doubt has been cast[12] on the correctness of this structure, since the other octahedrally coordinated first-row transition metal diiodides TiI_2, VI_2, MnI_2, FeI_2, and CoI_2 all have the cadmium diiodide type structure.)

NiI_2 becomes antiferromagnetic[13] at T_N = 75 K and the magnetic structure at 4.2 K has been determined[14] from ^{129}I Mössbauer studies. The structure consists of sheets of ferromagnetically coupled Ni atoms in (001) planes, with the spins along one of the Ni–I bonds and with an antiparallel arrangement from one plane to the next.

Free-Ion Spectrum

All the terms, except the ^1S term, belonging to the d^8 configuration of the free Ni^{2+} ion have been observed experimentally.[15] These term energies, which are given in Table I, cannot be described accurately using the theoretical Condon–Shortley expressions, due to the neglect of configuration interaction in the theory. Ferguson et al.,[16] reviewing parameters fitted to the spectrum, have derived the most reliable values. With these, the agreement between theory and experiment is good for all the levels, except for the ^1G term (see Table I), and the ratio of the electron repulsion parameters is close to the theoretical value.

Table I. Energy Levels (cm^{-1}) of Free Ni^{2+} Ion

Term	Obsd[a] energy	Calcd[b] energy	Obsd[c] energy of center of gravity	Theor[c] formula of center of gravity
$^3F_4$	0	0	0	0
$^3F_3$	1 361	1 357		
$^3F_2$	2 270	2 269		
$^1d_2$	14 032	14 034	13 038	$5B + 2C$
$^3P_2$	16 662	16 726	15 847	$15B$
$^3P_1$	16 978	16 987		
$^3P_0$	17 231	17 244		
$^1G_4$	23 109	21 667	22 115	$12B + 2C$

[a] Reference 15. [b] Reference 16; calculated with B = 1042 cm^{-1}, C = 4060 cm^{-1}, and ζ = 668 cm^{-1}. [c] Relative to center of gravity of ^3F ground state.

The shortcomings in the theoretical formulation of the free-ion energy levels will be carried over into the calculations of the ligand field states of Ni^{2+} complexes, unless the free-atom representation[17] is used. If the weak-field or strong-field matrices are used in the conventional manner and B and Dq are fixed from the spin-allowed transitions, the value of C being determined from the spin-forbidden transitions to the $^1E_g(^1D)$ and $^1T_{2g}(^1D)$ states, the calculated energies of the transitions to the levels derived from the ^1G state will be in error. Although this analysis is widely employed, difficulties or errors in assignments can ensue, and the free-atom representation[17] seems clearly preferable.

Experimental Section

Anhydrous NiI_2 was prepared from nickel carbonate and concentrated hydriodic acid, as described by McPherson et al.[2] Crystals were grown from melts in a Bridgeman-Stockbarger furnace. Boules formed with cleavage planes approximately parallel to the axis of the silica tube and were easily cleaved with a razor blade along these planes, which are perpendicular to the crystallographic c axis, giving shiny black crystal plates of the desired thickness. Due to the hygroscopic nature of this compound, crystals were always handled in a drybox filled with nitrogen. The spectra were recorded at various temperatures, between 5 and 300 K, in the spectral range 4000–15 000 cm^{-1} using a Beckman Acta MIV spectrophotometer. In all cases the incident light was propagated parallel to the crystallographic c axis. Freshly cleaved crystals were clamped over circular apertures in brass plates and inserted in the sample chamber of an Oxford Instruments CF 200 continuous-flow liquid helium cryostat. Temperatures were determined and controlled to within ±2 K with an Oxford Instruments VC 30 temperature controller.

Due to crystal softness, micrometer measurements of thickness were not very accurate. However, a plot of thickness against the room-temperature peak intensity of the broad absorption at ≃7500 cm^{-1}, for eight different crystals with thicknesses ranging from ≃10 to 45 μm, resulted in satisfactory linearity (deviations <15%), giving molar absorptivities ϵ to 15%, from

$$\epsilon = AM/l\rho$$

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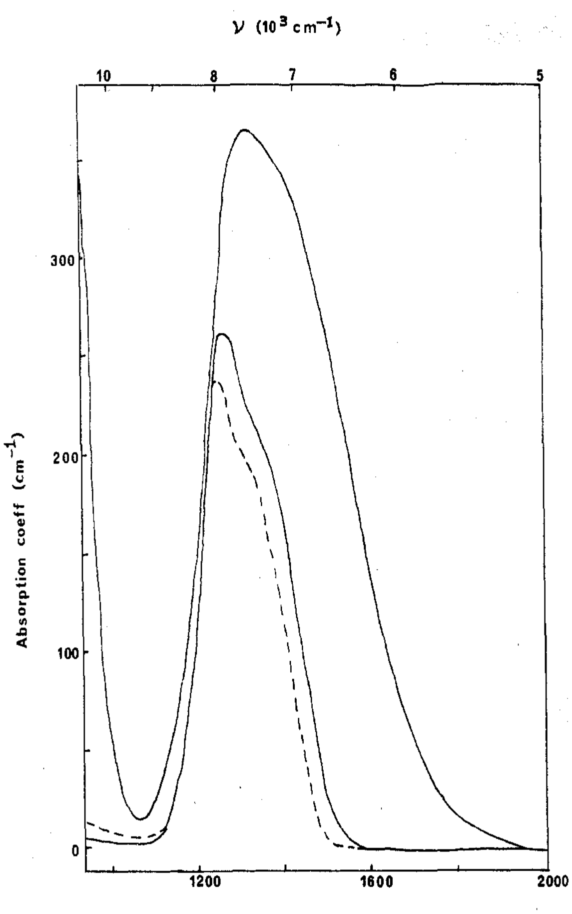

Figure 1. Presumed intervalence and $^3T_{2g}(^3F)$ absorptions in NiI_2. Above 1130 nm the curves are: top, 300 K; middle, 77 K; bottom, 5 K. Below 1130 nm there is an inversion: top, 300 K; middle, 5 K; bottom, 77 K.

A is the absorbance, M is the molar mass (312.5 g mol^{-1}), l is the thickness, and ρ is the density[18] (5.834 g cm^{-3}).

The integrated intensities from the band areas by planimetry gave the oscillator strengths f from

$$f = 4.32 \times 10^{-9} \int_{\nu_1}^{\nu_2} \epsilon \, d\nu$$

where ϵ is the molar absorptivity and ν is the wavenumber in cm^{-1}. Because of errors in baseline determination and in thickness and area measurements, as well as overlapping with adjacent bands and the charge-transfer absorption, the oscillator strengths are accurate to $\simeq$30%, but relative values are accurate to within 15%.

The near-infrared absorption was decomposed into Gaussian components from replotted absorbance vs. wavelength spectra, by resolution with a du Pont 310 curve resolver.

Results

At room temperature the absorption spectrum of NiI_2 shows only an asymmetric intense band centered at $\simeq$7500 cm^{-1} before the onset of charge-transfer absorption at $\simeq$10 000 cm^{-1}, as shown in Figure 1. This broad band can be resolved into two Gaussian components with maxima at 7100 and 7900 cm^{-1}. As the temperature is lowered, the charge-transfer edge shifts to higher energies revealing an intense broad band centered at 12 120 cm^{-1} with a low-energy shoulder at 11 270 cm^{-1} at 70 K (Figure 2). At this temperature the near-infrared absorption has approximately halved in intensity, as seen in Figure 1, and the lower energy Gaussian component has shifted to 7300 cm^{-1}, whereas the position of the other component is virtually unchanged. Further cooling, to 5 K, shifts the higher energy broad band to 12 200 cm^{-1} and resolves the shoulder into two sharp lines at 11 165 and 11 260 cm^{-1}, and the charge-transfer edge now occurs at $\simeq$13 000 cm^{-1} (Figure 2). The near-infrared absorption is further decreased in intensity and has Gaussian components with maxima at 7375 and 8000 cm^{-1} at this temperature (Figure 1).

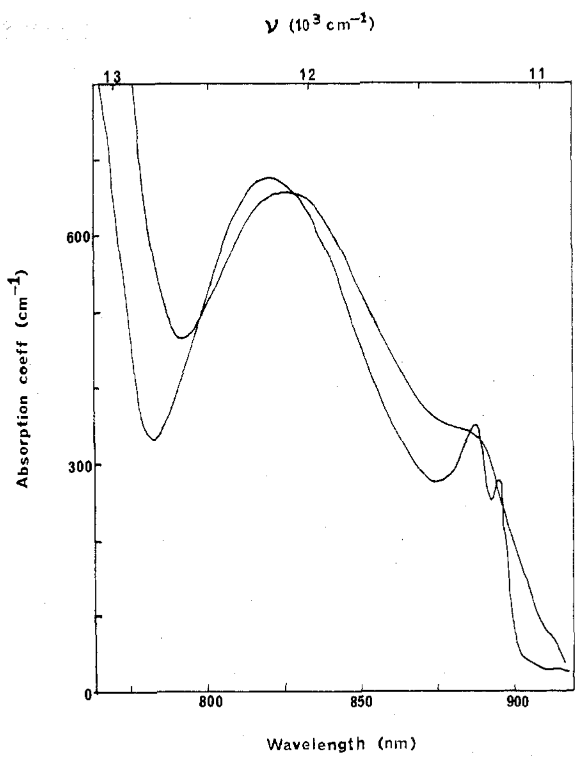

Figure 2. $^3T_{1g}(^3F)$ and $^1E_g(^1D)$ absorptions in NiI_2: upper, 70 K; lower, 5 K. (At 300 K the main charge-transfer band completely obscures this region.)

Table II. Observed and Calculated Energies (cm^{-1}) and Oscillator Strengths in the 5 K Absorption Spectrum of NiI_2

Assign	Energy		Oscillator strength
	Obsd	Calcd[a]	
$^3A_{2g}(^3F) \rightarrow {}^3T_{2g}(^3F)$	7 375[b]	7 400	2.9×10^{-5}
CT[c]	8 000[b]		3.9×10^{-5}
$^3A_{2g}(^3F) \rightarrow {}^1E_g(^1D)$	11 165 11 260	11 240	2.0×10^{-5}
$^3A_{2g}(^3F) \rightarrow {}^3T_{1g}(^3F)$	12 200	12 090	1.8×10^{-4}

[a] Calculated with Dq = 740 cm^{-1} and the term energies expressed as the following percentages of the free-ion values: ^3P, 65%; ^1D, ^1G, 70%. [b] These are maxima of the Gaussian components of the absorption centered at 8000 cm^{-1}. [c] For discussion of this transition, see text.

Table II summarizes the observed maxima and oscillator strengths at 5 K.

Discussion

Assignment of Spectra of NiF_2, $NiCl_2$, and $NiBr_2$. Before assigning the observed absorptions in the spectrum of NiI_2, consideration should be given to band assignments in the spectra of NiF_2 and particularly $NiCl_2$ and $NiBr_2$, which have the same crystal structure as NiI_2. There is[1] considerable disagreement concerning the assignments for $NiCl_2$ and $NiBr_2$, partly due to the use of the strong-field formalism. Attempts to resolve these differences have been made here by calculating the transition energies using the free-atom representation, since, as indicated under "Free-Ion Spectrum", calculations made in the conventional way cannot accurately reproduce the energies of all the spin-forbidden transitions.

The calculated energies were obtained by computer diagonalization of the crystal field energy matrices and are shown together with the observed energies in Table III. Spin–orbit

Table III. Calculated and Observed Energy Levels (cm^{-1}) Relative to $^3A_{2g}(^3F)$ Ground State for NiF_2, $NiCl_2$, and $NiBr_2$

	NiF_2		$NiCl_2$		$NiBr_2$	
State	Calcd[a]	Obsd[b]	Calcd[c]	Obsd[d]	Calcd[e]	Obsd[d]
$^3T_{2g}(^3F)$	7 450	7 450	7 700	7 700	7 550	7 540
$^3T_{1g}(^3F)$	12 600	12 770–13 020	12 770	11 800, 12 700	12 350	≃12 300 to ≃13 300
$^1E_g(^1D)$	14 260	15 075–15 220	13 350	≃13 800	12 830	
$^1T_{2g}(^1D)$	21 390	21 300–20 800	20 430	20 200	19 820	19 841
$^1A_{1g}(^1G)$	23 950		21 800		20 630	≃16 600[f]
$^3T_{1g}(^3P)$	24 330	24 450–24 150	22 540	22 600	20 920	≃20 900
$^1T_{1g}(^1G)$	28 020	28 200	26 500	27 200		
$^1E_g(^1G)$	32 840	32 000	31 670	30 200		
$^1T_{2g}(^1G)$	33 520		32 290			

[a] Calculated with $Dq = 740$ cm^{-1} and the following values of the term energies expressed as percentages of the free-ion values: ^3P, 92%; ^1G, 93%. An effective ^1S term energy of 35 500 cm^{-1} was used. [b] Observed maxima from 300 K spectrum.[22] [c] Calculated with $Dq = 770$ cm^{-1} and the following values of the term energies expressed as percentages of the free-ion values: ^3P, 77%; ^1D, 84%; ^1G 85%. An effective ^1S term energy of 30 600 cm^{-1} was used. [d] Observed maxima from 5 K spectrum.[3] [e] Calculated with $Dq = 755$ cm^{-1} and the following values of the term energies expressed as percentages of the free-ion values: ^3P, 67%; ^1D, 80%; ^1G, 81%. An effective ^1S term energy of 28 000 cm^{-1} was used. [f] Tentative assignment.

coupling was neglected and the effective term energies, appropriately reduced from the free-ion values to give the best fit, were substituted directly into the weak-field matrices[19] for a d^8 ion in an O_h symmetry ligand field. However, the free-ion energy of the ^1S term is not known[15] and the derived $^1A_{1g}$ ligand field state is obscured in NiF_2, $NiCl_2$, and $NiBr_2$ by charge-transfer absorption in the region where it is expected to occur. Since the theoretical formulation underweights electron correlation effects,[20,21] the term is predicted[20] to be well below 51 000 cm^{-1} calculated using the Racah parameters needed to fit the other d^8 terms. From the position of the $^1A_{1g}(^1S)$ state of $KNiF_3$ the ^1S energy was fixed[20] at 35 500 cm^{-1}, this value being adopted here for NiF_2, together with 30 600 and 28 000 cm^{-1} for $NiCl_2$ and $NiBr_2$, respectively. The energies adopted do not greatly influence the energies of the $^1A_{1g}(^1G)$ states.

Agreement between calculated and observed energies for the ligand field transitions in the spectra of NiF_2, $NiCl_2$, and $NiBr_2$ is good, as shown in Table III. The assignments given here for NiF_2 are in agreement with those made by Balkanski et al.[22] except for the transition to the ^1E_g, $^1T_{2g}(^1G)$ levels.[1] For $NiCl_2$ and $NiBr_2$, the assignments differ[1] in some cases from those previously given, but the present calculations appear to provide the best description of the observed spectra. The exception is the system of sharp bands centered at ≃16 600 cm^{-1}, in the spectrum of $NiBr_2$, which is not at all well represented by the present calculations, or indeed any other. This absorption has no equivalent in the spectrum of $NiCl_2$ and has previously been identified as either $^3A_{2g}(^3F) \rightarrow {}^1E_g(^1D)$ or $^3A_{2g}(^3F) \rightarrow {}^1T_{2g}(^1D)$. As our calculations now preempt these possibilities, we provisionally choose the nearest calculated level for the transition, viz., to the $^1A_{1g}(^1G)$ state (Table III), though vibrational overtones or impurity absorption are not precluded (as noted by a referee).

Assignment of NiI_2 Spectrum. By comparison with other NiX_2 dihalide spectra, the NiI_2 broad band at 12 100 cm^{-1} is assigned to the spin-allowed $^3A_{2g}(^3F) \rightarrow {}^3T_{1g}(^3F)$ transition and the sharp lines at 11 165 and 11 260 cm^{-1} to the spin-forbidden $^3A_{2g}(^3F) \rightarrow {}^1E_g(^1D)$ transition.

Assignment of asymmetric broad lower energy absorption is at first sight problematic, since it is resolvable into Gaussian components separated at 5 K by ~600 cm^{-1} and is thus not simply a spin-allowed transition to $^3T_{2g}(^3F)$. Attributing these to the splitting of the O_h T_{2g} state into $^3A_{1g}$ and $^3E_{2g}$ components by the actual D_{3d} symmetry at Ni^{2+} is not tenable, in view of the symmetrical appearance of the equivalent bands of $NiCl_2$ and $NiBr_2$, which are only slightly less trigonally distorted than NiI_2.

Transmission spectra of Kel-F grease mulls of NiI_2 at 77 K[2] matched our single-crystal observations at 70 K, except that the sharp lines at 11 200 cm^{-1} were missing. Similar $CsNiI_3$ spectra[2] showed a broad band at 6500 cm^{-1} with a narrower one at 8000 cm^{-1} and another broad band at 11 000 cm^{-1}. The broad absorptions were assigned[2] to the spin-allowed transitions to $^3T_{2g}(^3F)$ and $^3T_{1g}(^3F)$, respectively, and the narrow band was tentatively taken as the spin-forbidden $^3A_{2g}(^3F) \rightarrow {}^1E_g(^1D)$ transition. If this were right, then the NiI_2 absorption at 8000 cm^{-1} should be similarly assigned but now at the cost of understanding the origin of the sharp ~11 200-cm^{-1} lines. Furthermore, the 8000-cm^{-1} NiI_2 band seems too broad for such an intraconfigurational (thus sharp) transition, both states arising from the $t_{2g}{}^6e_g{}^2$ (strong-field) configuration.

Since this band is difficult to assign to a ligand-field transition, we have considered the following intervalence charge-transfer (CT) transition as a possibility:

$$\left\{\begin{array}{c} Ni^{2+}I^- \\ \updownarrow \\ Ni^+I^0 \end{array}\right\} + Ni^{2+}I^- \xrightarrow{h\nu} \begin{array}{l} Ni^+I^- + Ni^{2+}I^0 \qquad (1) \\ \qquad\text{or} \\ Ni^{2+}I^0 + Ni^+I^- \qquad (2) \end{array}$$

The extreme left-hand-side species represents CT resonance; the two alternatives given on the right imply net intervalence transitions of either $I^0 + I^- \rightarrow I^- + I^0$ or $Ni^+ + Ni^{2+} \rightarrow Ni^{2+} + Ni^+$. Both should be of quite low energy, Franck–Condon considerations indicating the latter to involve the higher energy; to distinguish them is difficult but fortunately not necessary. Evidence for believing this transition to occur is obtainable from consideration of ionization potentials I: VI_2,[23,24] MnI_2,[25] and FeI_2[8,26] show no equivalent low-energy CT spectra, and the second ionization potentials for $M^+(3d^n) \rightarrow M^{2+}(3d^{n-1})$ (adjusted for the electronic redistribution $M^+(3d^{n-1}4s) \rightarrow M^+(3d^n)$ in Mn and Fe) are 18.15, 15.95, 14.65, and 13.86 eV for Ni, Fe, V, and Mn, respectively, indicating that the intervalence transition, forming a net M^+, will have the lowest energy in NiI_2 compared with other MI_2. In support of such reasoning we would expect the energies of the *primary* CT bands to fall in the I-predicated sequence, and at 5 K the primary CT edges are indeed observed to fall at 13 000 (NiI_2), 15 000 (FeI_2[8]), 25 000 (VI_2[23]), and 33 000 (MnI_2[25]) cm^{-1}, respectively. Temperature dependence (below) provides further support.

If the assignment of the 8000-cm^{-1} band is correct, then the peak at 7375 cm^{-1} can be confidently assigned to the $^3A_{2g}(^3F) \rightarrow {}^3T_{2g}(^3F)$ transition. Thus, $Dq = 740$ cm^{-1} for NiI_2, and, using this value and the reduced free ion term energies shown in Table II, the energies of the other observed transitions can be calculated and are shown to be in good agreement (Table II). Due to the small number of observable bands in the spectrum, the values of the term energy reductions are not very reliable. This applies particularly to the ^3P and ^1G terms, since ligand field states arising from them are not observed and they

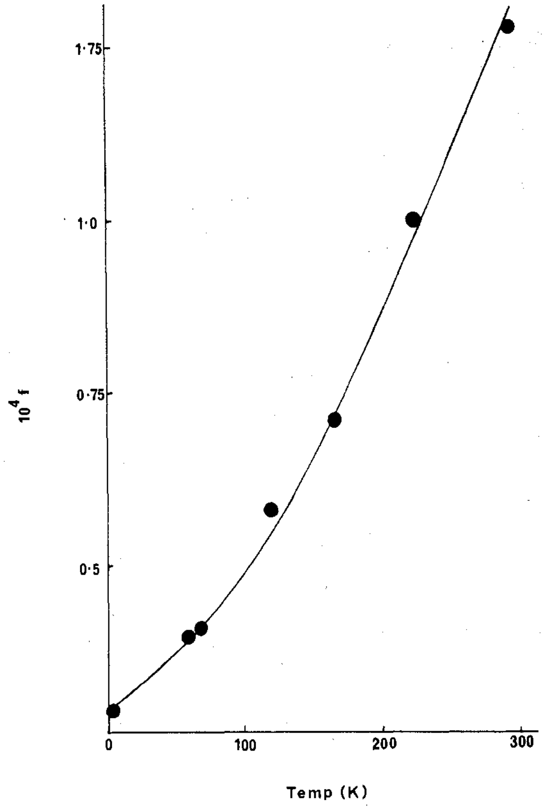

Figure 3. Temperature dependence of oscillator strength f of $^3T_{2g}(^3F)$ absorption.

only slightly influence the energies of the transitions to the $^3T_{1g}(^3F)$ and $^1E_g(^1D)$ states, respectively, through configuration interaction. However, the effective energies used in the fitting appear reasonable on comparison with the respective values used in the fitting of the other NiX_2 spectra.

Intensities and Temperature Dependence. The $^3A_{2g} \to {}^3T_{1g}(^3F)$ transition is obscured or overlapped strongly by the charge-transfer edge at temperatures above 70 K, and thus little information can be deduced regarding its temperature dependence. However, the $^3A_{2g}(^3F) \to {}^3T_{2g}(^3F)$ transition can be studied throughout the entire temperature range and is observed to narrow (half-width 1500 cm^{-1} at 300 K and 900 cm^{-1} at 6 K) and shift to higher energies as the temperature is reduced, due to the cooling out of absorptions resulting from "hot" exciton–phonon combinations.[1] A plot of its oscillator strength against temperature, Figure 3, confirms that it gains intensity by a vibronic mechanism, since the temperature dependence resembles a hyperbolic cotangent function.

Overlapping with the spin-allowed $^3A_{2g}(^3F) \to {}^3T_{1g}(^3F)$ transition and the charge-transfer edge also precludes any detailed measurements of the temperature dependence of the intensity of the $^3A_{2g}(^3F) \to {}^1E_g(^1D)$ transition. As with $NiCl_2$ and $NiBr_2$,[3,4] no sharp change in its intensity was observed at the Nêel temperature,[13] $T_N = 75$ K, such as that found for the spin-forbidden transitions in $FeCl_2$ and $FeBr_2$, which are metamagnetic like NiI_2, where there was a contribution to the intensities from an exciton–magnon "hot"-band mechanism. The $^3A_{2g}(^3F) \to {}^1E_g(^1D)$ transition showed[3-5] no exchange-induced enhancement of intensity in $NiCl_2$ or $NiBr_2$ (both metamagnetic) unlike some of the other spin-forbidden transitions. However, comparison of the oscillator strength of this transition in NiI_2 ($f \simeq 2 \times 10^{-5}$) with those[3] in $NiCl_2$ and $NiBr_2$ ($f \simeq 6 \times 10^{-7}$) shows that it is appreciably more intense in the diiodide. The following are possible causes. A novel cooperative mechanism[3,4,27] may have arisen; the NI_6 may simply be more covalent, or, roughly equivalently, intensity may have been gained from the near (within 2000 cm^{-1}) CT transition (cf. 20 000- and 10 000-cm^{-1} separations from CT bands in $NiCl_2$ and $NiBr_2$[3-5]); or, finally, the greater spin–orbit coupling to I, cf. Br or Cl, could be responsible, as suggested[23,25] for VI_2 and MnI_2, where the CT bands are too distant to allow borrowing. Insofar as the enhanced intensities have hitherto been associated with iodide, the spin–orbit coupling mechanism seems responsible.

The band at $\simeq$8000 cm^{-1}, which has been tentatively assigned to a charge-transfer transition (1) or (2), narrows as the temperature decreases (half-width 950 cm^{-1} at 300 K and 600 cm^{-1} at 5 K). However, its oscillator strength ($f \simeq 3.9 \times 10^{-5}$) remains apparently constant, within experimental error, throughout the entire temperature range. Such behavior is further evidence that this absorption does not arise from a transition to a component of the $^3T_{2g}(^3F)$ state, since such a transition would be expected to show a vibronic-type temperature dependence. The temperature independence of the intensity of this absorption indicates that there is no thermal equilibrium between Ni^+I^0 species, since the intensity would then decrease with temperature. Thus Ni^+I^0 implies a low-weighted term in the ground-state wave function predominantly represented by $Ni^{2+}I^-$.

Finally, the main argument for following a ligand field (discrete-ion) formulation follows from the clear demonstration[28] that, in the *gas-phase* dihalides MX_2, the bonding is predominantly ionic, an important[29] conclusion equally applicable to the solids.

Registry No. NiI_2, 13462-90-3; NiF_2, 10028-18-9; $NiCl_2$, 7718-54-9; $NiBr_2$, 13462-88-9.

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