The Single-crystal Spectrum of Transitions to ^1G States of Nickel(II) in Distorted Tetrahedral Environments

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Temperature-dependent and polarized spectra of transitions to excited states arising from the ^1G free-ion term are reported for single crystals of $(Et_4N)_2NiCl_4$ and $(Et_4N)_2NiBr_4$. The resolved fine structure of one band at 5 K is interpreted in terms of progressions in the symmetric modes. The results suggest that these hitherto unutilized bands could be of importance in establishing the nature of the co-ordination of nickel ions in less exactly defined environments, and they are used here to give some insight into the change in geometry of the $NiCl_4^{2-}$ and $NiBr_4^{2-}$ units as the temperature is lowered.

MOST low-temperature, single-crystal electronic spectra of nickel(II) in tetrahedral and distorted tetrahedral environments have been obtained from ions doped into host lattices.[1-3] The main advantages of such samples are that the host lattices are sufficiently hard to form good optical faces and the absorbance of the most intense levels can readily be controlled by using a fairly low concentration of chromophore. As a consequence the intense levels have been studied thoroughly and the rather weak transitions to excited states arising from the ^1G free-ion term have been largely neglected.

Recently[4] we carried out a complete ligand field calculation for tetragonally distorted tetrahedral nickel(II) and assessed the sensitivity of each level of the system to changes in the environment. The relative splittings of levels arising from the ^1G free-ion term in a tetragonal field are particularly sensitive both to the ligand field strengths and to the degree of distortion from tetrahedral symmetry and in fact the width of the band manifold of these levels would represent the best measure of the degree of distortion. It appeared to us that a full study of these levels should be undertaken, partly because they lie in the visible region of the spectrum and would offer a means of characterizing more exactly the many nickel complexes for which the near-i.r. bands are obscured by the nature of the media and partly because the utility of the complete calculation can only be assessed when as many transitions as possible have been properly defined.

Studies of ion-doped systems are difficult to interpret since the environment surrounding the impurity ion is not necessarily the same as the equivalent point in the host lattice and, at present, there is no way of establishing accurately the difference between them. Pure compounds of tetrahedral nickel(II) on the other hand tend to be soft and often moisture-sensitive so that it is difficult to obtain samples sufficiently thin for an accurate spectroscopic study of the most intense transitions but, with careful preparation, they are suitable for an investigation of the weaker ones. We chose to study the

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[1] T. W. Couch and G. P. Smith, *J. Chem. Phys.*, 1970, **53**, 1336.

[2] H. A. Weakliem and D. S. McClure, *J. Appl. Phys.*, 1962, **33**, 347.

[3] R. Pappalardo, D. L. Wood, and R. C. Linares, jun., *J. Chem. Phys.*, 1961, **35**, 1460.

[4] A. Mooney and W. E. Smith, *J.C.S. Dalton*, 1973, 287.

spectra of $(Et_4N)_2NiCl_4$ and $(Et_4N)_2NiBr_4$ for which we have been able to solve the sample handling techniques sufficiently well to allow a complete room-temperature visible spectrum to be taken.

The structure of $(Et_4N)_2NiCl_4$ was determined by Stucky *et al.*[5] The space group is $P4_2/nmc$. The site symmetry of the Ni^{2+} is D_{2d} and the major axes of the $NiCl_4^{2-}$ ions are aligned along the four-fold axis of the crystal. The structure at low temperatures is uncertain, particularly because a phase change is indicated at 220 K.[6] The bromide, for which no evidence of a phase change has been reported, is assigned to the same room-temperature structure as the chloride from cell-constant data.

The spectra of transitions to states other than those arising from the ^1G term are rather similar to spectra for equivalent ion-doped samples, but owing to the high intensity of some of the bands we did not carry out a thorough spectral analysis in these cases. It was possible however to fit the calculation to the rather sharp low-energy band edges at 5 K, and hence to predict the approximate energy values of the transitions to ^1G states. The relative splittings within the ^1G free-ion term for both tetrahedral and tetragonal perturbations are shown in Figure 1. The actual energy positions calculated in a previous paper [4] are used to aid in assigning the spectra. The spin–orbit states in D_{2d} symmetry are given with the tetrahedral orbital assignments in parentheses. Where vibrational fine structure is analysed, the vibrations are given in terms of the D_{2d} point group with the tetrahedral equivalent in parentheses.

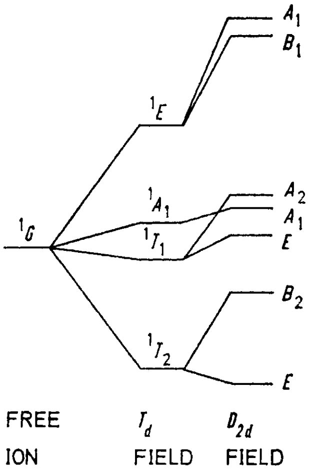

FIGURE 1 Relative splittings within the ^1G free-ion term

The $A_1(^3T_1,^3F)\rightarrow B_2,E(^3A_2,^3F)$ band in the near-i.r. region is partially resolved at 5 K and has already been analysed [7] in terms of the symmetric modes $A_1(\nu_1)$ and $A_1(\nu_2)$. In pure compounds it is reasonable to compare these excited-state vibrational modes with the results obtained for the ground state by Raman spectroscopy and we discovered good agreement between the two. A similar approach is used for the more complex progression analysed here.

EXPERIMENTAL

Crystal preparation and growth were by standard methods. The crystals were oriented by use of the polarizing microscope, the orientation was checked by taking oscillation and Weissenberg photographs, and the crystals were then mounted on silica discs and polished down to give an optic axis section. The final orientation was checked by use of the microscope as a conioscope.

To obtain the full range of data, we required two instrument systems. At temperatures down to 100 K a simple liquid-nitrogen cryostat equipped with heaters and a chromel–alumel thermocouple was used in conjunction with a double-beam SP1800 spectrometer. The results give a relatively accurate measure of absorbance required for oscillator strength measurements. Below 100 K, an Oxford Instruments modular Dewar vessel equipped with a variable-temperature cold-finger attachment was used with a single-beam Monospek D400 monochromator and a photomultiplier detection unit. This instrument is capable of high-resolution measurements and, to ensure that heating effects were kept to a minimum, the cryostat was mounted between the monochromator and detector so that only monochromatic radiation fell on the sample.

The sample holder and sample edges up to the optical path were covered with a thermally conducting, non-transparent, grease to ensure good thermal contact between them and the sample block. In all cases, the temperature quoted is the temperature of the block.

The sample size was typically 4 mm × 2 mm and with the exception of the most intense ^3P bands for which some reference compensation was used, the maximum absorbance of sample and holder recorded in any run on the SP 1800 instrument was less than 2·0. It is difficult to be as exact with the single-beam instrument which measured transmission, but we are confident that the samples were sufficiently thin to allow the measurement of the ^1G spectra correctly.

For the chloride crystal, there is already evidence of a phase change at 220 K [6] and we find that an irreversible increase in baseline occurs at about this temperature. In the case of the bromide, we have observed a very small baseline change which appears to occur reasonably consistently at *ca.* 255 K, but it is not sufficiently large to appreciably to alter the interpretation of the spectrum and substantiating evidence from other techniques would be required before any conclusion regarding a phase change in the bromide could be made.

The most likely explanation of the baseline change in the chloride was that the crystals cracked at the phase change. A microscopic investigation of a number of samples which had been cycled through the phase change showed that there was a crazing effect just observable microscopically in some but not all samples. We concluded that a submicroscopic cracking occurred in the other samples. It was not possible to prevent this effect by slowing down the cooling rate, but the room-temperature polarization ratio is not appreciably affected by cycling the crystal through

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[5] G. D. Stucky, J. B. Folkers, and T. J. Kostenmacher, *Acta Cryst.*, 1967, **23**, 1064.

[6] M. Gerloch and R. C. Slade, *J. Chem. Soc.* (*A*), 1969, 1012.

[7] A. Mooney, R. H. Nuttall, and W. E. Smith, *J.C.S. Dalton*, 1972, 1096.

the phase change so that, although the crystals may crack on cooling, the orientation is retained throughout.

The baselines of the chloride spectra do not change appreciably with temperature on either side of the discontinuity at the phase change but the bromide baseline shows a gradual rise between 255 and 100 K and the effect is reversible, indicating a change in the refractive index of the crystal.

DISCUSSION

The overall spectrum of both samples at 300 K and the calculated energy positions are shown in Figure 2.

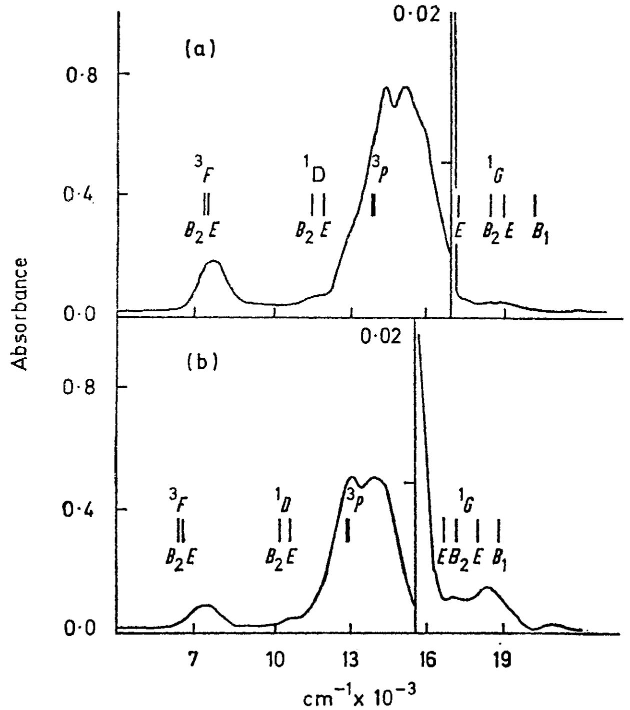

FIGURE 2 Near-i.r.–visible spectra of (a), $(Et_4N)_2NiCl_4$ and (b), $(Et_4N)_2NiBr_4$ at 300 K. Approximate calculated energy positions of the electronic origins are indicated

Since the calculation was carried out to predict the approximate no-phonon positions at 5 K and there are no intense hot bands in tetrahedral Ni^{2+}, the calculated positions are on the low energy side of the bands. We were interested to check that the intensities of the bands in pure materials were similar to those for systems containing isolated tetrahedral nickel(II) ions either in solution or solid, but it is difficult to measure accurately either the thickness of the film or the absorbance of the most intense bands. The values obtained for the most intense peaks (350 ± 50 and 400 ± 50 l mol^{-1} cm^{-1} for the chloride and bromide respectively) are in good agreement with the values for doped systems within the error of the measurement. The intensity of transitions to ^1G states are very weak and are more intense in the bromide than the chloride, features which are also in good agreement with solution studies.

The calculation predicts that the ground state for both compounds is a spin–orbit A_1 with the E state *ca.* 150 cm^{-1} higher in energy. There is evidence that this is substantially correct for the chloride.[6,7] Since the spectra of the two compounds are rather similar and extreme values of the distortion parameters would be required for a well separated E ground state, it seems that this prediction is also correct for the bromide.

Selection Rules.—The spin selection rule is broken by spin–orbit coupling which mixes some triplet character into the singlet wave functions. In principle, transitions to levels arising from the ^1D free-ion term should be more intense than those to the ^1G term, since direct mixing between the ^1D and ^3P is expected and in first order the ^1G functions mix only with the ^3F which is much further away in energy. This prediction is borne out by the chloride spectrum (Figure 1) but the bromide is much less convincing and in fact, owing to second-order mixing, the eigenvectors of the ^1G functions from the complete calculation show that there is considerable ^3P character in the ^1G functions in both cases [*e.g.*, 3·4% in the $B_2(^1T_2,^1G)$ function for the chloride, 4·0% for the bromide].

Since the orbital selection rules for tetrahedral Ni^{2+} are complex and often misunderstood, we restate the basic position. Using the standard approach for molecules, we separate the vibronic integral[8] (1) into two integrals (2) and (3). To a first approximation integral

$$\rho = \int \Psi_{ev}{}^{*} O_p \Psi_{ev}{}' \mathrm{d}\tau \qquad (1)$$

$$\rho = \underset{(2)}{\int \psi_e{}^{*} O_p \psi_e{}' \mathrm{d}\tau} \,.\, \underset{(3)}{\int \psi_v{}^{*} \psi_v{}' \mathrm{d}\tau}$$

(2) is zero for all electric dipole transitions between d-orbital states since the wave functions of both states will have even parity. If however, the Ni^{2+} lies in a non-centrosymmetric point group, some odd-parity wave character may be mixed into the state as, for example, in T_d symmetry the $(Y_3{}^2 + Y_3{}^{-2})$ spherical harmonics in the crystal-field potential will mix $3d$ and $4p$ wave functions. In general, owing to symmetry and energy considerations, there will be a different degree of mixing in each state so that the integral (2) need not, strictly, be zero and we therefore interpret our spectra in terms of relatively intense electronically allowed transitions and weaker forbidden transitions requiring vibronic selection rules. The details are in Table 1.

Polarized Spectra.—At room temperature and at slightly lower temperatures we obtained polarization data which could not be reproduced at 5 K, but which are in general agreement with the very weak spectra obtained by Couch and Smith[1] for these bands in nickel-doped Cs_3MgCl_5 at 5 K.

The chloride samples which gave similar polarization data at all temperatures studied down to the phase

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[8] G. Hertzberg, ' Molecular spectra and molecular structure,' vol. III, Van Nostrand, New York, 1965, p. 128.

change are illustrated at 240 K (Figure 3) where there is least overlap with the ^{3}P spectrum. The lowest-energy transition expected from the calculation is to an orbitally degenerate $E(^1T_2)$ state which would be allowed, polarized σ. Since this state is subject to a Jahn–Teller distortion, the transition may not obey the simple polarization rules and may exhibit more than one maximum.[9] It is difficult to estimate the relative intensities of the lowest-energy band in both polarizations, but certainly it appears quite strongly in both. The next allowed transition is to a $B_2(^1T_2)$ state, which should be polarized π and the maximum polarization difference between the more intense π spectra and the σ occurs at an energy position close to that expected from the calculation of the band origin position. These two states would be degenerate in a tetrahedral environment and their separation is one of the most noticeable effects of the tetragonal distortion.

TABLE 1

Selection rules for transitions to ^1G states. Where a symmetry-forbidden transition is made allowed by a vibration, the symmetry of the vibration is written to indicate this

Type of selection rule	Operator symmetry	Excited state				
		A_1	A_2	B_1	B_2	E
Symmetry	z (π)	—	—	—	Allowed	
Allowed	$x\ y$ (σ)	—	—	—	—	Allowed
Symmetry	z (π)	—	$\nu_2(B_1)$	—	—	$E(\nu_3)E(\nu_4)$
Forbidden	$x\ y$ (σ)	$E(\nu_3)E(\nu_4)$	$E(\nu_3)E(\nu_4)$	$E(\nu_3)E(\nu_4)$	$E(\nu_3)E(\nu_4)$	$B_1(\nu_2)B_2(\nu_3)B_2(\nu_4)$

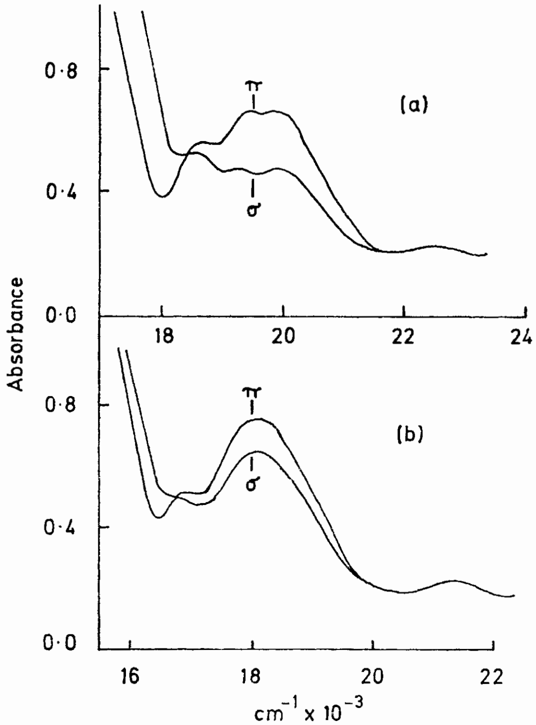

FIGURE 3 Polarized spectra of the transitions to levels arising from the ^1G free ion term (π = parallel to z; σ = perpendicular up z); (a), $(Et_4N)_2NiCl_4$ at 233 K; (b), $(Et_4N)_2NiBr_4$ at 300 K

A subtraction of the σ from the π spectrum suggests that the $A_1 \rightarrow B_2(^1T_2,^1G)$ transition is rather broad and its maximum does not correspond to any of the three peaks in the σ spectrum. The first two are probably due to the Jahn–Teller split $A_1 \rightarrow E(^1T_2,^1G)$ transition but the third may be part of the $A_1 \rightarrow E(^1T_1,^1G)$ transition which should also be Jahn–Teller-distorted. In D_{2d} symmetry, both transitions are allowed but in T_d only the former is and therefore in view of the small distortion from tetrahedral geometry in this compound it is likely that the $A_1 \rightarrow E(^1T_1,^1G)$ transition will be relatively weak. The calculated position is in agreement with this assignment of the third peak and a weak, resolved band at 5 K in about the correct energy position further confirms this (Figure 6).

The highest-energy band in both materials is due to an $A_1 \rightarrow A_1,B_1(^1E,^1G)$ transition which is forbidden in both T_d and D_{2d} symmetry and since the allowing vibrations are different for the σ and π spectrum it should be, but is not, polarized. The maximum intensity of the individual components of this band will occur at some vibrational amplitude of the allowing vibration. It is clear from the crystal structure that the chloride ions have a high thermal ellipse and the $NiCl_4^{2-}$ unit could well pass through the tetrahedral position during the course of the vibration. It seems that the maximum transition probability may occur close to this position.

The polarization effect in the bromide is smaller and greatest at the highest temperature. For the room-temperature spectrum (Figure 2) the preceding arguments for the chloride are applicable again, although there is no evidence for the $A_1 \rightarrow E(^1T_1,^1G)$ band, which is only observed close to 5 K.

Fine Structure.—Both crystals were cooled to 5 K to obtain the vibrational–electronic fine structure of as much of the spectra as possible. The Monospek D400 instrument was used and, where it proved critical, care was taken to obtain the highest possible resolution. The bromide spectra were consistently sharper than those for the chloride over several runs with different samples.

The best-resolved band was the spin- and orbitally-forbidden $A_1 \rightarrow A_1,B_1(^1E,^1G)$ level of the bromide

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[9] M. D. Sturge, *Solid State Phys.*, **1967**, **20**, **91.**

(Figure 4). It is interpreted in terms of only one electronic origin since the percentage triplet character is much higher in the B_1 state and the A_1 level is predicted to lie underneath the poorly resolved high-energy side of the band envelope. The full analysis is shown in Figure 4 and appears to be unique; no other combination of selection rules and vibrational progressions can give an approximate fit.

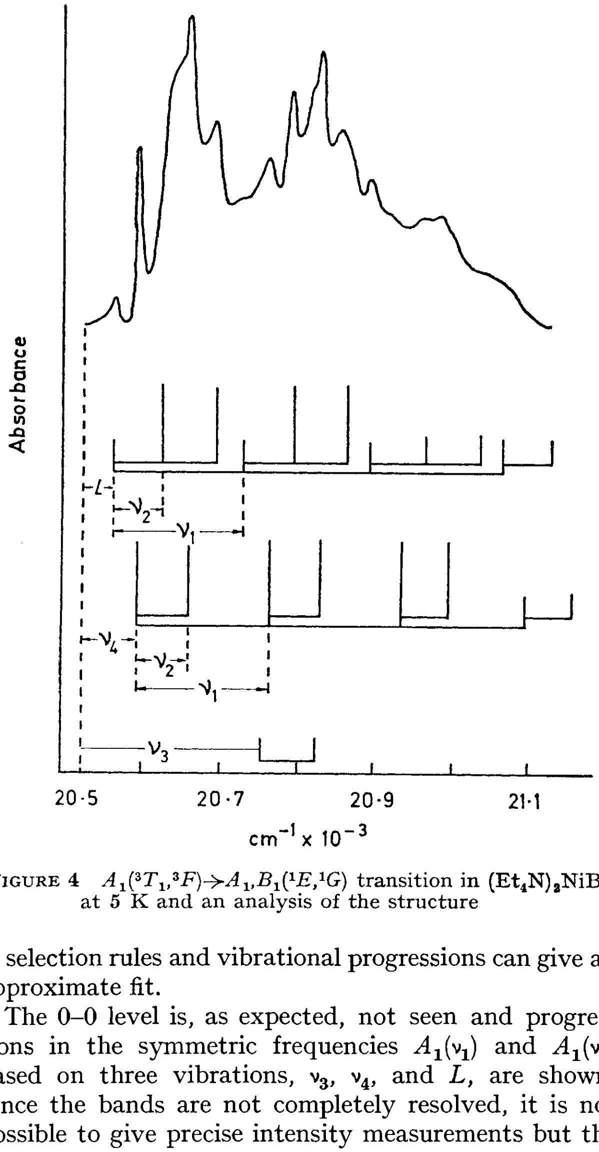

FIGURE 4 $A_1(^3T_1,^3F)\rightarrow A_1,B_1(^1E,^1G)$ transition in $(Et_4N)_2NiBr$ at 5 K and an analysis of the structure

The 0–0 level is, as expected, not seen and progressions in the symmetric frequencies $A_1(\nu_1)$ and $A_1(\nu_2)$ based on three vibrations, ν_3, ν_4, and L, are shown. Since the bands are not completely resolved, it is not possible to give precise intensity measurements but the heights of the lines in the analysed progressions indicate the approximate intensity of the assigned peaks and show a consistent pattern throughout. The actual frequencies, together with differences to demonstrate the accuracy of the analysis, are in Table 2. The overall band shape, in contrast to the allowed case, shows a maximum some distance from the origin. The vibrational intervals correspond to $\nu_1 = 165 \pm 7$ cm^{-1} and $\nu_2 = 68 \pm 7$ cm^{-1}, which are in remarkably good agreement with the ground-state Raman frequencies[7] ($\nu_1 = 168$ cm^{-1} and $\nu_2 = 73$ cm^{-1}).

The frequencies of the allowing vibrations in the ground state were obtained from a study of the far-i.r. powder spectrum of the complex. The ν_3 vibration is at 225 cm^{-1}. There is a bad discrepancy between the powder measurements[10] for the chloride and the single-crystal reflectance spectrum[11] with regard to the ν_4 band. Since the bromide spectrum is similar we inferred its true position, from a comparison with the chloride data, as 70 cm^{-1}. The splitting of ν_3 and ν_4 owing to the low symmetry field is less than 2 cm^{-1} in the chloride and since we obtained no evidence of any splitting in the powder data of the bromide it seems that the splitting in it is also small. We therefore do not expect to resolve the spectrum due to B_2 and E components of the ν_3 and ν_4 tetrahedral vibrations in the visible spectrum. A factor-group analysis shows that there are a considerable number of lattice vibrations which could be the vibration L but, as might be expected for lattice vibrations closely spaced in energy, we obtained only one broad band with a maximum at 40 cm^{-1}.

TABLE 2

Assignments of the vibrational electronic components in the $A_1\rightarrow B_1(^1G)$ transition of $(Et_4N)_2NiBr_4$. Differences between levels are given in columns 4 and 5 against the level with the highest vibrational quanta in each case

Allowing vibration	No. of quanta of ν_1 and ν_2	Energy/ cm^{-1}	Differences $\Delta\nu_2$	Differences $\Delta\nu_1$
L		20,567		
	$+\nu_2$	20,648sh	81	
	$+2\nu_2$	20,699	51	
	$+\nu_1$	20,725		158
	$+\nu_1 + \nu_2$	20,794	69	
	$+\nu_1 + 2\nu_2$	20,855	61	
	$+2\nu_1$	20,898		173
	$+2\nu_1 + \nu_2$	20,964	66	
	$+2\nu_1 + 2\nu_2$	21,040	76	
ν_4		20,597		
	$+\nu_2$	20,661	64	
	$+\nu_1$	20,768		171
	$+\nu_1 + \nu_2$	20,833	65	
	$+2\nu_1$	20,920		152
	$+2\nu_1 + \nu_2$	20,990	70·	
	$+3\nu_1$	21,070		150
ν_3		20,752		
	$+\nu_2$	20,818	66	

Obviously, since we do not observe the no-phonon peak, a direct comparison of the i.r. frequencies with the values used to fit the spectra is not possible, but the differencies between the frequencies should correlate. $\nu_4 - L$ from the i.r. data is 30 cm^{-1} and from the visible spectrum 30 cm^{-1}, and $\nu_3 - L$ from the i.r. data is 195 cm^{-1} and from the visible spectrum is 185 cm^{-1}. The inaccuracies both of the i.r. technique and the fitting of the visible spectrum, being borne in mind, this is a good correlation.

The spectra for the chloride are less detailed, and a similar but simpler analysis, given in Figure 5, fits the main bands. Two progressions, based on ν_3 and ν_4, are

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[10] A. S. Sabatini and L. Sacconi, *J. Amer. Chem. Soc.*, 1964, **86**, 17.

[11] J. Dunsmuir and A. P. Lane, *J. Chem. Soc. (A)*, 1971, 2781.

postulated, with the most intense levels being progressions in $A_1(\nu_1)$. Obviously the interpretation is not as definitive as for the bromide and the most intense components do not correspond to the same number of vibrational quanta, but the interpretation is at least in general agreement with it.

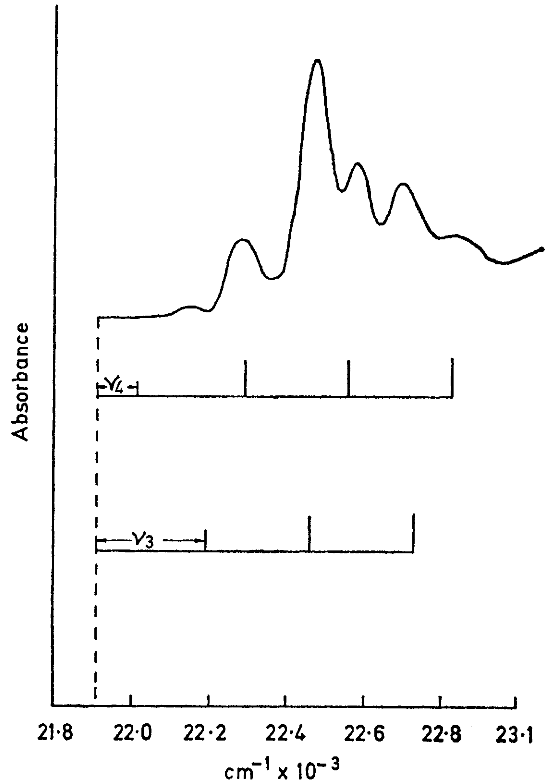

FIGURE 5 $A_1(^3T_1,^3F)\rightarrow A_1,B^1(^1E,^1G)$ transitions in $(Et_4N)_2NiCl_4$ at 5 K

The low-energy orbitally allowed $A_1\rightarrow E(^1T_2,^1G)$ band is also partially resolved and in this case the first two levels are split by 19 cm^{-1}. There is no progression in the spectrum of 19 cm^{-1}, so that we interpret these two levels as the Jahn–Teller-split components of the E state. The entire spectrum is similar to the examples given by Sturge[9] for comparable transitions in other systems. Two poorly resolved progressions in ν_2, one based on each of the 19 cm^{-1} split peaks, are observed (Table 3). It is unfortunate that $\nu_1 \approx 3\nu_2$ for the bromide so that, at this degree of resolution, a progression in ν_1 could not be identified.

The shapes of the bands at 5 K confirm much of the previous argument concerning the selection rules. The $A_1\rightarrow B_2,E(^3A_2,^3F)$ near-i.r. transition analysed in a previous paper[7] is an example of an orbital- and spin-allowed transition and the chloride shows a classical profile for such a transition with the most intense level appearing at the lowest-energy, presumably 0–0, position. This profile suggests that the ground- and excited-state potential wells have minima at about the same distance from the nucleus. The bromide on the other hand shows a slight rise away from the origin suggesting that the excited-state minimum is slightly displaced with respect to the ground state, as might be expected for the more polarizable ligand. The orbital- and spin-forbidden level analysed in this paper has the classic shape for a forbidden transition, rising smoothly to a maximum away from the band origin.

TABLE 3

Assignments of the vibrational electronic components in the $A_1\rightarrow E(^1G)$ transition of $(Et_4N)_2NiBr_4$. Differences between levels are given in column 3 against the level with the highest vibrational quanta in each case

No. of quanta of ν_2	Energy/cm^{-1}	Difference $\Delta\nu_2$
	16,540	
ν_2	16,608	68
$2\nu_2$	16,680	72
$3\nu_2$	16,750	70
	16,559	
ν_2	16,631	72
$2\nu_2$	16,711	80
$3\nu_2$	16,776	65
$4\nu_2$	16,836	60

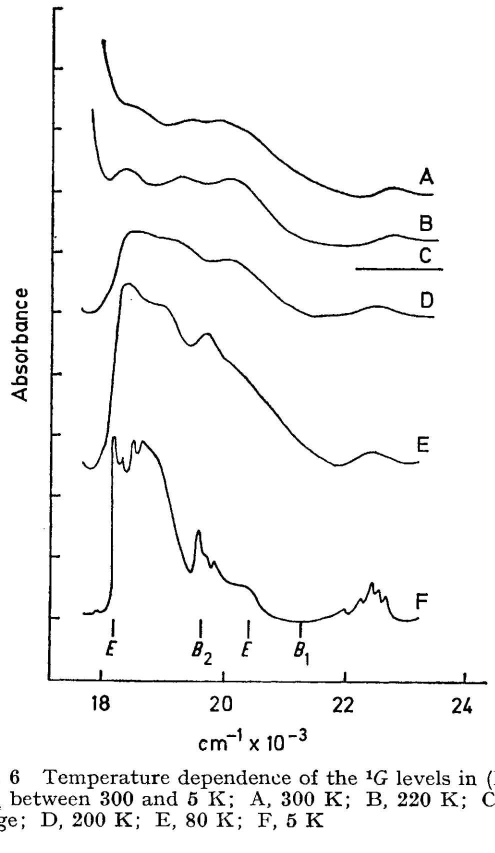

FIGURE 6 Temperature dependence of the ^1G levels in $(Et_4N)_2$-$NiCl_4$ between 300 and 5 K; A, 300 K; B, 220 K; C, phase change; D, 200 K; E, 80 K; F, 5 K

It is interesting that in all bands studied the progression intervals predict values of ν_1 and ν_2 for their respective excited states which are not much different from the ground-state values obtained from the Raman spectrum, suggesting that there is little relaxation of the potential wells of the excited states compared with the ground state. The use of an electronic calculation based on one centre is therefore reasonable, since if the excited states were really ' exciton ' levels involving some delocalization, a considerable relaxation of the frequencies would be expected.

Temperature Dependence.—Two marked effects occur in the spectrum of the chloride as it is cooled through the phase change (Figure 6). There is a sharp irreversible change in the baseline, presumed to be due to sample cracking, and the clear polarization effect is lost, but reversibly.

The latter effect suggests a sudden reorientation of the $NiCl_4^{2-}$ units or a change in the bond angle as do Gerloch and Slade's[6] magnetic anisotropy measurements where it was found that the difference in $\mu_{\parallel}$ and $\mu_{\perp}$ was smaller below the phase change than above it. Remarkably, the energy positions and shape of the unpolarized spectrum are little altered by the phase change.

Between 300 and 200 K, the energy separation of the highest- and lowest-energy bands decreases, suggesting a gradual change to a more tetrahedral environment, but, close to the temperature of the phase change, there is no shift in energy comparable either with the loss of polarization or the magnetic anisotropy change. It seems more likely that a reorientation of the $NiCl_4^{2-}$ ions occurs rather than any sudden change of bond angle. Recently e.s.r. data[12] on single crystals of $(Et_4N)_2ZnCl_4$ doped with $CoCl_4^{2-}$ and on $(Et_4N)_2CoCl_4$[13] have demonstrated that below the phase change the ions remain tetragonally distorted and aligned but the unique axis is reoriented. Since the nickel salt is isostructural, a similar result would be expected and the interpretation given here is in agreement with those observations.

In the temperature range 200—100 K the intensity of the ^1G spectrum increases more rapidly than in the temperature ranges above or below this so that it seems that the reorientation process is more complex than that suggested.

In the bromide sample (Figure 7) there is again some decrease in the separation of the highest- and lowest-energy bands between 300 and 200 K, but the temperature dependence of the polarization effect is even more complex. It decreases with decreasing temperature, but by 100 K the direction of polarization is reversed. We have checked this on a number of samples and are confident that, although the effect is small, the $A_1 \rightarrow B_2(^1T_2, ^1G)$ transition is polarised σ rather than π at 100 K. We obtained no polarization at 5 K. The baseline shows a gradual but reversible rise between 300 and 100 K probably owing to a change in the refractive index of the crystal. We conclude that the molecules reorient in a manner analogous to the chloride but the actual change in orientation direction is a complex process, occurring over a wide temperature range.

The calculation carried out previously required only one ^1G level to be assigned (to fit the Trees correction α). The lowest-energy band edge was chosen for this purpose and so the actual calculated band origin position of all other levels are predictive results. In the present analysis only their approximate positions have so far been used. The main argument has concerned selection rules, band shapes, and, where possible, polarization results and so it is of interest to compare the 5 K spectrum with the calculated positions.

For the chloride, the agreement between the spectrum and the calculation is remarkably good and the assignment of the $A_1 \rightarrow B_2(^1T_2, ^1G)$ transition is in agreement with positions predicted from the polarization measurements at high temperatures. For the bromide there is a considerable discrepancy, particularly in the fitting of the $A_1 \rightarrow A_1, B_1(^1E, ^1G)$ transition. We are confident that the assignment of the resolved band at *ca.* 20,500 cm^{-1} to this transition is correct, since no other single-centre transition is expected in this energy region and the bromide and chloride spectra of this band are remarkably similar in that they resolve, and have similar shapes and relative intensities. The very weak band at *ca.* 19,000 cm^{-1} has been confirmed by studies of very thick samples. It is probably due to either the $A_1 \rightarrow A_2(^1T_1, ^1G)$ or

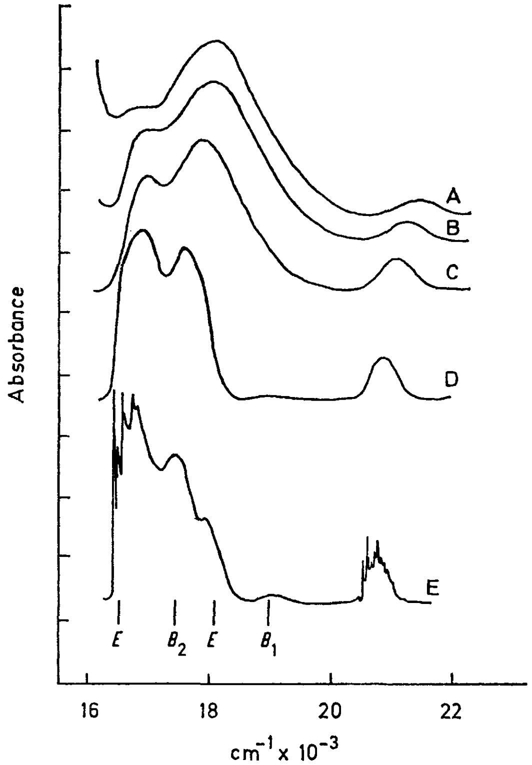

FIGURE 7 Temperature dependence of the ^1G levels in $(Et_4)N_2NiBr_4$ between 300 and 5 K; A, 300 K; B, 220 K; C, 100 K; D, 42 K; E, 5 K

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[12] G. E. Shankle, J. M. McElearney, R. W. Schwartz, A. R. Kampf, and R. L. Carlin, *J. Chem. Phys.*, 1972, **56**, 3750.

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$A_1 \rightarrow A_1(^1A_1,^1G)$ transitions, which are expected to be weak and lie close together in energy (Figure 1 and ref. 4). With these assignments, a larger value of Dq and a smaller value of D_T would fit the ^1G transitions better. There is no reason why Dq and D_T values chosen to fit transitions to other free-ion terms should be correct for ^1G transitions since the radial distribution functions will be somewhat different for each term, and the difference between terms may be greater for the more polarizable ligand. In view of the non-rigid geometry of the $NiBr_4^{2-}$ ion in this complex, however, further studies of other systems would be required before a failure in the theory could be confirmed.

It appears that the Jahn–Teller effect is greater in the chloride than the bromide. The shape of the band expected for a transition to a Jahn–Teller-distorted excited state is well known.[9] The bromide spectrum at 42 K gives the best defined example for that compound, since at 5 K the overall band shape is obscured by sharp fine structure. If it is assumed that the second peak is entirely due to the $A_1 \rightarrow B_2(^1T_2,^1G)$ transition, the shape of the first peak is exactly as expected for a fairly small Jahn–Teller effect. With larger Jahn–Teller effects subsidiary maxima would be expected, and in the chloride the first two peaks appear to belong to the $A_1 \rightarrow E(^1T_2,^1G)$ transition.

The actual separation between them increases as the temperature rises. The fact that we were unable to resolve and assign a subsidiary maxima in the bromide is, of course, only weak evidence but it is interesting that the shape of the high-temperature ^1G spectrum of two such similar compounds should be so different, whereas the ^3P spectra are rather similar. The explanation of a greater Jahn–Teller effect in the chloride explains the difference nicely, since only the E states of ^1G free-ion terms and the $E(^1D)$ would be expected to undergo a Jahn–Teller effect in D_{2d} symmetry.

The hot bands of the system are of very low intensity, and the only example noted with certainty is a weak level, resolved at 5 K, for the chloride only. It is more intense in Ni^{2+} in ZnO but even in that system remains fairly weak.

Conclusions.—The bands assigned span a large enough range of energies, and have sufficiently different shapes, intensities, and temperature dependences to suggest that they will give useful information about the structure of nickel complexes provided that enough examples of these ions in pure compounds can be studied. In this paper we have used the variation with temperature of the levels to explain at least in part the complex movement of the $NiCl_4^{2-}$ and $NiBr_4^{2-}$ entities as the temperature changes.

We have analysed the fine structure resolved on one band of one of the compounds and related it to the ground-state i.r. and Raman spectra. The progression is in terms of symmetric modes. There is little relaxation between ground and excited states as measured by the change in frequency between the vibronic and the vibrational values for ν_1 and ν_2.

The selection rules were evaluated on the basis of orbitally allowed and orbitally forbidden transitions. The shapes of the bands, their intensities, polarization dependence, and positions as calculated by ligand field theory are in agreement with these selection rules.

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