b/a were obtained from Kahana's paper by a smooth extrapolation of his published values of a, b, and c for atomic radii of 2, 3, and 4 a.u. This process yielded values of c/a and b/a of 0.17 and 0.22, respectively, for lithium.

To estimate the accuracy with which the lengths of the radius vectors in the three principal directions could be determined by this experiment, a series of calculations was made using a phenomenological model of the Fermi surface. The model consisted of a sphere of radius r with 12 "bumps" superimposed toward the nearest zone boundaries. The size and shape of the bumps were varied by changing the values of the principal radii. For each set of principal radii, the areas of slices through the model Fermi surface normal to the principal directions were calculated. The distortion of the model was increased until the differences of the calculated areas exceeded the experimental error of the differences in the measured counting rates. In this manner it was concluded that a difference of 1.5% in the radii k_{110} and k_{100} would result in observable differences in the measured counting rates.

No attempt was made to place upper limits on the amplitude of the higher-momentum components and the size of the energy gap in sodium. Based on our experience with lithium, such estimates could be reliably obtained from the almost-free-electron approximation.

CONCLUSIONS

The principal conclusions from this experiment can now be restated as follows:

(1) The principal radii of the Fermi surface of sodium are equal within an estimated accuracy of 1.5%.

(2) The annihilation rate for electrons near the Fermi surface is about 20% greater than the rate for electrons near the origin, in substantial agreement with Kahana's calculation.

ACKNOWLEDGMENTS

It is a pleasure to thank Dr. D. M. Rockmore and Dr. J. H. Kusmiss for model calculations and Dr. W. B. Daniels for use of a furnace for growing sodium crystals.

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Lattice-Vibration Effects in the Spectra of ZnO:Ni and ZnO:Co

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The optical absorption spectra of ZnO:Ni^{2+} and ZnO:Co^{2+} have been studied in the visible region, at temperatures from 7°K up. From correlation with lattice phonon energies, evidence has been found for the assignment of much of the band structure to vibronic sidebands. For both crystals, some weak lines on the low-energy side of the bands have been shown by their concentration dependence to be due to transition-ion pairs. In ZnO:Ni, a level whose polarization shows it to be an A_1 appears 8 cm^{-1} above the strong E–$T_2(^3P)$ transition. It is suggested that the A_1 level is produced by the Jahn-Teller interaction.

1. INTRODUCTION

THE optical absorption spectra of transition-ion impurities in crystals often show more structure than expected from the static crystal-field model. Electron-lattice interaction[1,2] gives rise to absorption due to vibronic sidebands, with energy transfer to the host lattice as well as to the transition ion.[3] This sideband structure may be analyzed if the host lattice vibrations are known.

Previous work on the spectra of ZnO:Ni and ZnO:Co[4–6] has shown that satisfactory assignments can be made for the strong-field levels of cubic symmetry, but identification of spin-orbit components and the splittings produced by the small trigonal field is difficult. The present study of the spectra was undertaken to clarify the importance of the effects of low-symmetry fields, spin-orbit coupling, and vibronic interactions. Most of the spectra were taken at low resolution for convenience, but for sharp lines a higher-resolution instrument was used to supplement this. Results were taken at various temperatures from 7°K up, and polarization dependence and concentration dependence of the spectra were studied. No extensive theoretical analysis was attempted.

Section 2 describes the experimental procedures used. Section 3 gives the results obtained for the visible spectra of ZnO:Ni and ZnO:Co, and for some Zeeman measurements on the sharp lines of ZnO:Ni. In Sec. 4 an analysis of the ZnO:Ni results is presented, showing that the visible band has pronounced phonon structure.

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A trigonal crystal-field calculation is given, using all available data, which is just sufficient to allow determination of the parameters. A brief discussion is given of some pair lines found.[7] Section 5 covers the identification of some sharp lines in ZnO:Co by polarization and temperature dependence studies, and the sidebands in the spectrum are analyzed. As in ZnO:Ni, some lines due to transition-ion pairs are found. Section 6 discusses electron-lattice interaction effects in ZnO:Ni. One sharp line, which cannot be assigned on the basis of a static crystal-field model, can be explained using the dynamic Jahn–Teller effect,[8,9] and other effects in the crystal give evidence for the perturbation quenching described by Ham.[9,10] In conclusion, Sec. 8 discusses the importance of electron-lattice interaction effects in the spectra, and suggests some further possibilities for study.

2. EXPERIMENTAL

ZnO crystals were grown from lead fluoride flux,[11] using analytically pure chemicals. Varying percentages of transition-metal oxide, carbonate or nitrate were added to the melt to give crystals with different impurity concentrations. The melt percentage is used throughout this paper as a nominal crystal concentration, since the spectra showed that, apart from some weak lines, absorption intensity was proportional to melt concentration.

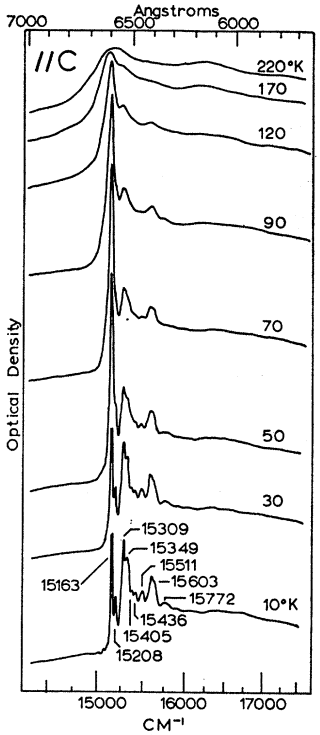

FIG. 1. Temperature dependence of the π spectrum of ZnO:Ni. The intense line at 15 163 cm^{-1} has been weakened due to low resolution. To lessen overlap, this line has been truncated for the two lowest temperatures.

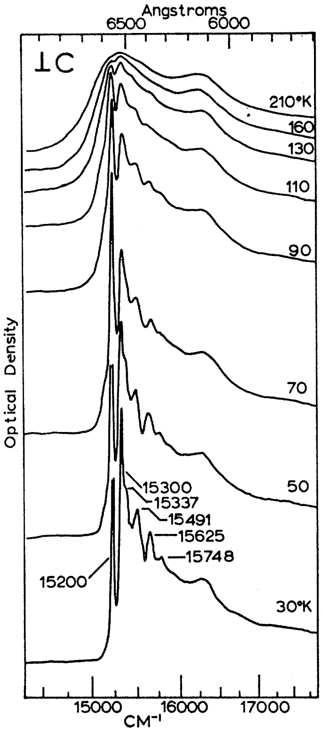

FIG. 2. Temperature dependence of the axial spectrum of ZnO:Ni. The spectrometer-weakened line at 15 200 cm^{-1} has been truncated for 50 and 30°K.

A range of crystals were grown. Most samples grew as thin hexagonal plates suitable for axial study, but occasionally usable dendritic side growths including the *c* axis direction were found. These could be used to obtain polarized spectra, but their small size (typically 0.7×1 mm) reduced the obtainable accuracy. The crystals found most useful for study were an axial plate of 0.16 mm thickness and an *a* axis dendritic growth 0.19 mm thick, both of 0.76% nominal Ni^{2+} concentration, and a ZnO:Co^{2+} crystal of 0.55% nominal concentration and 0.11-mm thickness. Unless otherwise stated, all spectra in this paper are taken for these crystals.

Over the range 4000–8000 Å, spectra were taken with resolution 10–30 cm^{-1} on a Bausch and Lomb Spectronic 505. For sharp lines, where this resolution was inadequate,[7,12,13] a Jarrell-Ash 3.4-m Ebert spectrometer was used in third order, giving resolution better than 0.3 cm^{-1} even with wide slits for maximum intensity. Absolute line positions could be found to 2 cm^{-1}.

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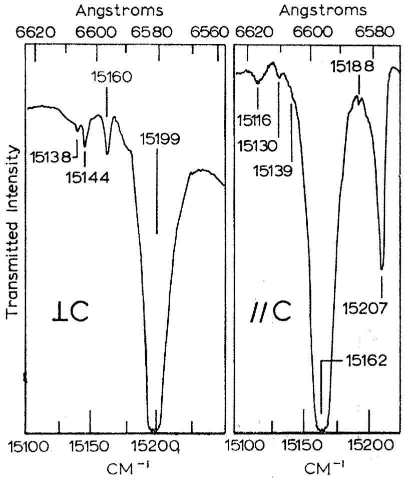

FIG. 3. The 15°K axial spectrum and 19°K π spectrum of ZnO:Ni recorded in absorption on the Jarrell-Ash spectrometer.

Low-temperature spectra were obtained using an Andonian associates variable temperature Dewar, in which samples could be held at any temperature from about 7°K to room temperature, with an accuracy of control and measurement better than 2°K. The sample and copper/constantan thermocouple were clamped to a 99.9%-purity copper block used as sample holder.

The restricted space and high beam convergence angle of the Spectronic 505 sample compartment precluded the use of a prism to obtain polarized light. Polaroid sheet of type HN38 was found to have adequate spectral response and selectivity over the range 5000–8000 Å. The sheet could be attached directly to an outer window of the Dewar, and aligned relative to the crystal before the Dewar was placed in the spectrograph.

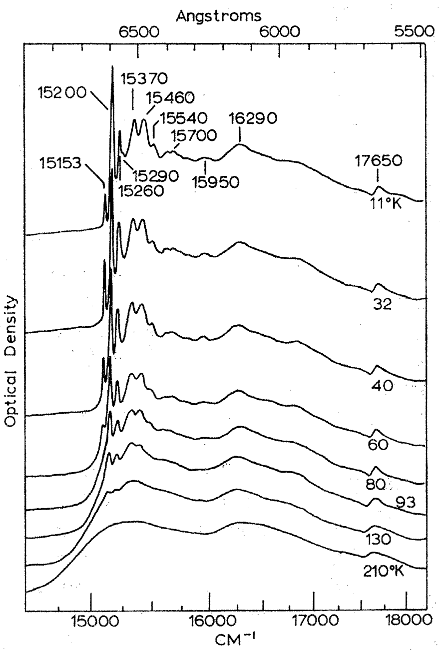

FIG. 4. Temperature dependence of the axial spectrum of ZnO:Co. At low temperatures, the lines at 15 260 cm^{-1} and below are weakened by resolution limiting.

3. EXPERIMENTAL RESULTS

A. ZnO:Ni

The spectra of ZnO:Ni in the 15 000–16 000 cm^{-1} region consists of sharp no-phonon lines at 15 200 cm^{-1} in σ polarization and 15 163 cm^{-1} in π polarization, with vibronic sidebands on the higher-frequency side. As previously reported,[6] the axial and σ spectra were found to be identical, verifying that the transitions are electric dipole in origin.[14] Figures 1 and 2 show the temperature dependence observed in the π and axial spectra using the Spectronic 505. The very intense 15 163 and 15 200 cm^{-1} lines reduce in apparent intensity on cooling because of resolution effects[12,13] as the lines narrow with decreasing temperature. Because of the complexity of the higher-energy structure of the band, temperature dependence is harder to define for the other components. The discrete peaks observed at low temperatures appear to widen and merge into each other, and the total oscillator strength of the visible band decreases with increasing temperature. This decrease could be due to thermal depopulation of the ground state to the first excited level[15] at 140 cm^{-1}.

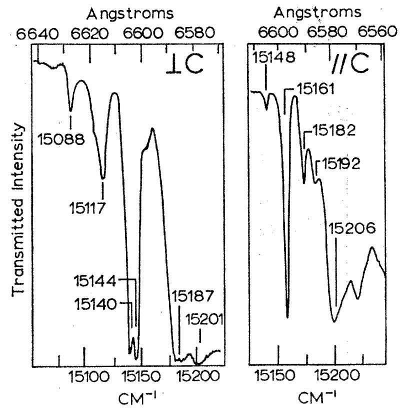

FIG. 5. The axial and π spectra of ZnO:Co at 7°K, recorded on the Jarrell-Ash spectrometer.

The axial and π spectra as taken on the Jarrell-Ash are shown in Fig. 3. Owing to the small size of the crystal, accuracy is low for the π spectrum. The weak lines which can be detected at low energy in Fig. 1 can be seen here more clearly. Using samples of nominal concentration 0.1, 0.5, and 0.76% of Ni^{2+}, it was found that the intensity of most of the weak lines of the axial

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spectrum is proportional to the square of the concentration of Ni^{2+}, as is characteristic of pair spectra. The 15 160-cm^{-1} line (Fig. 3) was an exception, showing intensity linear with concentration, indicating that this σ absorption is a transfer of intensity from π polarization.

The 15 208-cm^{-1} line in π polarization is not the same line as the 15 200-cm^{-1} line in σ, since the energy difference is consistently greater than the limits of error. The line shows the same temperature dependence as the two very strong lines.

Weakliem[16] has recently studied the Zeeman splitting of the 15 200- and the 15 300-cm^{-1} lines of the axial spectrum, using pulsed magnetic fields of up to 209 kG. He found that the 15 200-cm^{-1} line splits into two circularly polarized components, the lower of which shows a linear shift corresponding to a g value about half that of the free ion, while the other component has a nonlinear shift. The 15 300-cm^{-1} line gives roughly twice the splitting with polarization directions in the opposite sense, though in this case the maximum splitting is of the order of the linewidth and accuracy will be lower. Crystal-field calculations show that the cubic field E level should be in this vicinity, but the predicted splitting order is opposite to that observed, and the variation of energy of the two components as the field changes does not agree with theory. This discrepancy must be accounted for if the 15 300-cm^{-1} line is to be assigned as $E-E(^3P)$.

B. ZnO:Co

Fewer data were obtained for ZnO:Co than for ZnO:Ni, as the dendritic sample used for the polarization study was too heavily absorbing for good spectra to be obtained on the Spectronic 505. However, good axial spectra were obtained, and high-resolution spectra were taken for all polarizations. Figure 4 gives the temperature dependence of the axial spectrum, showing that as for ZnO:Ni, the lowest-energy lines are sharper and more marked in temperature dependence than the rest of the spectrum. The high-resolution spectra of Fig. 5 show that the sharp axial lines both contain two components, with some weak lines at lower energy. The variation of intensity of the axial lines in samples of nominal concentration 0.17, 0.55, and 1.0% of Co^{2+} showed that the weak lines were due to pairs. The energies of the lines in the 1% sample are shown in Fig. 6. For the lower concentrations, the line positions were the same. Most of the weak π lines are probably due to pair interaction also. Some lines may, like the 15 160-cm^{-1} line of ZnO:Ni, be single-ion lines with polarization borrowing.

TABLE I. Known peaks in the energy distribution of lattice phonons in pure ZnO. Energies are in cm^{-1}, the assignments are those of the original references. The first two columns are for phonons of zero wave vector, the last column gives phonons of nonzero k found by multiphonon absorption.

Reference 20	Reference 22	Reference 23
101 E_2		101 TA_2
		137 TA_1
	180 $TO_3(E_2)$	
		243 LA
380 A_1	383 $TO_2(E_2)$	
407 E_1	420 $TO_1'(A_1)$	426 TO_2
437 E_2	438 $TO_1(E_1)$	441 TO_1
	538 LO_2	489 LO
574 A_1		
583 E_1	588 LO_1	

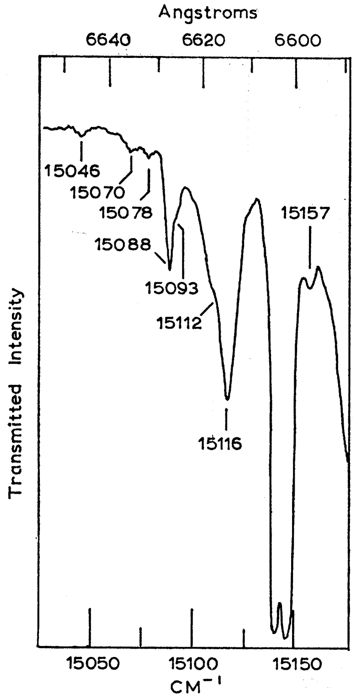

FIG. 6. The 10°K axial spectrum of a ZnO crystal containing nominally 1% of Co^{2+}. The lines indicated are shown to be pair lines by their intensity variation over a range of concentrations.

4. DISCUSSION OF ZnO:Ni RESULTS

The energy-level scheme and selection rules for d^8 in a tetrahedral field are given by Weakliem.[6] Of the four tetrahedral field components of the ^3P band, only a T_2 gives an allowed electric dipole transition from the A_1 ground state. Since the field contains a trigonal component, the other levels will become allowed to some extent, and the two T levels will split into A and E components. We may, however, expect that the A_1 and E components of the cubic allowed T_2 level will be the most prominent features of the ^3P band. These can be immediately identified as the 15 163- and the 15 200-cm^{-1} lines in π and σ, respectively. These and the 15 208-cm^{-1} component show widening and marked decrease of integrated intensity with increasing temperature, indicating that the lines are

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[16] H. A. Weakliem (private communication, 1966).

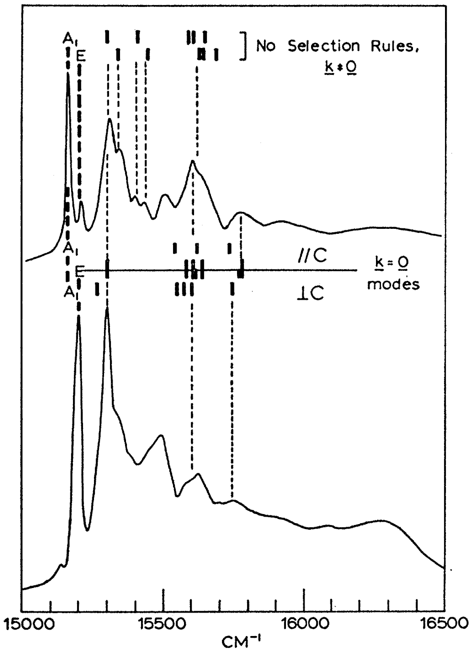

FIG. 7. Comparison of the ZnO:Ni polarized spectra at 10°K with the expected positions of lattice-phonon sidebands, taking the two strong lines at 15 163 and 15 200 cm^{-1} as no-phonon lines. The phonon energies are given in Table I.

no-phonon lines. It can be seen that the higher-energy components, even the relatively sharp line at 15 300 cm^{-1}, do not show this temperature dependence so markedly. They are also much less regular in shape, and polarization is not so definite. This, together with the fact that there is more structure than crystal field theory predicts, suggests that vibration excitation is taking place, as has been reported in other wurtzite crystals.[17–19]

Local modes round an impurity ion can have a much greater effect than lattice modes, particularly if the impurity ion is very different in mass from the ion it replaces. Ni^{2+} and Zn^{2+} are similar in mass and size, so local-mode effects are expected to be negligible here. The ZnO lattice mode frequencies found by Raman[20–22] and infrared[23,24] techniques can therefore be compared directly with spectral intervals observed, to determine vibronic sidebands. The polarization data available enables the sidebands corresponding to Raman modes to be verified by the factor-group selection rules,[25] in so far as these are applicable.[9] Table I gives the known lattice modes of pure ZnO. The sideband structure expected for these modes with the A_1 level at 15 163 cm^{-1} and the 15 200-cm^{-1} E level as no-phonon lines is shown in Fig. 7 for σ and π polarizations, and compared with the spectra. The strong 15 300-cm^{-1} line is a good energy fit for an E_2 sideband of the E level, suggesting that the line is vibronic in origin. In the similar system ZnS:Ni, there is a similar line 63 cm^{-1} above the narrow and intense line of the cubic field T_2 level,[6] and the E mode energy is 73 cm^{-1}.[17] While this agreement is only fair, the identification of the line as a sideband is still valid. One unexplained feature of the ZnO:Ni spectrum is the absence of an E_2 mode sideband on the A_1 level. This vibronic line should appear at 15 263 cm^{-1} in the σ spectrum.

The remainder of the band has reasonably distinct structure within the range of single-phonon energies, but beyond this there is little definite structure, further suggesting that most of the band is of single-phonon origin. It can be seen that most of the spectral components fit the host lattice modes. The 37-cm^{-1} splitting of the no-phonon lines is repeated, within the experimental error, in the 15 309–15 349- and 15 405–15 436-cm^{-1} pairs in the π spectrum, and the actual positions fit the phonons at 137 and 243 cm^{-1}. Near 15 600 cm^{-1} a cluster of lattice modes fits the large absorption in both polarizations, and the highest-energy modes are observed above this. Only the 15 491-cm^{-1} band in σ and the 15 511 cm^{-1} in π cannot be fitted. They may be associated with another electronic transition.

Further evidence for the vibronic origin of the 15 300-cm^{-1} line comes from the Zeeman results.[16] A magnetic field reduces the $3m$ symmetry to 3. Under this, the E representation is split into two parts E^+ and E^-, which transform as $x+iy$ and $x-iy$. The field separates the two components of the electronic level, but leaves the phonon energy unaltered. The product representations for the vibronic levels are $E^\pm \times E^\pm = E^\mp$, and $E^+ \times E^- = A$, the identity. The level E^+ and the E^- phonon component will transform as A, and so π polarization is allowed. With the E^+ phonon, the product representation is E^-, so the vibronic line in σ polarization will have a circular polarization opposite to that of its parent line. The argument for the E^- electronic level is the same. As the axial magnetic field is increased, the no-phonon line will split into two levels of opposite circular polarization. The vibronic lines will also split by the same amount in π and σ polarizations. In σ, the splitting will be in the opposite sense to the no-phonon line splitting, as observed by Weakliem. His 15 290-cm^{-1} line does, however, show roughly twice the splitting of the 15 200-cm^{-1} line. In spite of this discrepancy the 15 300 cm^{-1} will be assumed to be a vibronic, since the sense of the splitting

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TABLE II. Trigonal-field energy levels for d^8 in nearly tetrahedral symmetry, calculated to fit the observed spectrum of ZnO:Ni. The parameter-dependence figures are obtained by first-order perturbation theory.

Energy (cm^{-1})		Assignment of upper level		Change in energy for 1-cm^{-1} change in parameter					
Obs	Calc			Δ	v	v'	λ	B	C
	15 756	A_1	$^3T_1(P)$	0.08	0.00	−0.05	−1.54	6.82	0.01
	15 566	A_2	T_1–$^3T_1(P)$	0.08	0.17	−0.45	−0.96	6.82	0.00
	15 563	E		0.08	−0.10	0.17	−0.96	6.79	0.00
	15 381	E	$^3T_1(P)$	−0.04	−0.13	0.04	−1.24	5.43	0.35
15 200	15 264	E	T_2–$^3T_1(P)$	0.01	0.15	−0.37	−0.48	6.11	0.18
15 163	15 226	A_1		0.04	−0.14	0.38	−0.18	6.30	0.12
	13 543	E	$^1E(D)$	−0.47	−0.30	−0.27	2.00	0.00	1.65
	12 992	E	T_2–$^1T_2(D)$	−0.50	0.16	0.10	0.94	−1.27	1.81
	12 668	A_1		−0.52	0.44	0.59	0.42	−1.71	1.85
8 343	8 680	E	T_2–$^3A_2(F)$	1.16	0.00	0.09	−0.58	−7.94	0.01
	8 669	A_1		1.16	0.00	0.12	−0.48	−7.92	0.02
	4 694	A_2	$^3T_2(F)$	0.20	−0.16	0.00	−0.84	−8.00	0.00
	4 598	E		0.17	−0.32	−0.04	−0.38	−7.96	0.00
	4 414	A_2		0.18	−0.02	−0.16	−0.14	−7.98	0.00
	4 399	A_1		0.19	0.13	−0.16	0.12	−7.93	0.01
4 248	4 375	E		0.18	0.15	−0.04	−0.22	−7.96	0.01
4 217	4 259	E		0.19	0.18	0.00	0.10	−7.99	0.00
	1 421	A_1	T_2–$^3T_1(F)$	−0.67	−0.49	−0.63	−0.38	−7.74	0.00
	1 295	E		−0.65	−0.48	−0.60	0.32	−7.76	0.00
	863	E	$^3T_1(F)$	−0.66	0.28	0.38	−0.40	−7.80	0.00
260	372	E	T_1–$^3T_1(F)$	−0.66	0.21	0.33	1.58	−7.82	0.00
140	141	A_2		−0.66	0.35	0.61	2.06	−7.83	0.00
	0	A_1	$^3T_1(F)$	−0.67	0.22	0.39	2.80	−7.83	0.00

is wrong if the line is assigned to the $E-E(^3P)$ level, which should occur at about this energy.[16]

We may conclude that almost all of the structure in the visible bands can be assigned to lattice phonon sidebands of the levels of the cubic allowed $T_2(^3P)$ electronic state. This would be confirmed if corresponding bands were found on the low-energy side of the no-phonon lines in emission,[3] but attempts to obtain fluorescence in these crystals were unsuccessful.

Since only two identified transitions in the ^3P band are available for crystal-field fitting, trigonal field calculations are of limited use. A fit was tried, using as data the splitting of the $T_2(^3P)$ lines and the position of the A_2 first excited state.[15] The crystal-field parameter set Δ, v, and v' was used,[26] and the values of Δ, λ, B, and C as found by Weakliem[6] for the best fit of the cubic field were assumed, i.e.,

$$\Delta = 4200\ \mathrm{cm}^{-1},$$

$$\lambda = -250\ \mathrm{cm}^{-1},$$

$$B = 770\ \mathrm{cm}^{-1},$$

$$C = 3700\ \mathrm{cm}^{-1}.$$

Table II shows the best fit obtained, for the trigonal parameters

$$v = -470\ \mathrm{cm}^{-1},$$

$$v' = -200\ \mathrm{cm}^{-1}.$$

The first-order change in the energy of each level for unit change in each parameter is also given. With the present limited data it was not worthwhile trying to improve the fitting.

The weak lines below 15 200 cm^{-1} can from their concentration dependence be taken as due to interaction of pairs. Pair lines have been found in ZnS:Mn,[7] but the coupling was due to spin-spin interaction, using a coupling term $J\, \mathbf{S}_1 \cdot \mathbf{S}_2$ between ions 1 and 2. This interaction cannot contribute in ZnO:Ni, since spin is quenched in the ground state and the term will be zero unless two ions are excited simultaneously. The nature of the interaction in the present case is uncertain. Since the lines are close to the strong no-phonon lines, the perturbation involved is not large, and a small crystal field variation produced by the presence of a transition ion as a next-nearest neighbor may be sufficient to give the necessary shift. The absolute oscillator strength of the lines cannot be determined

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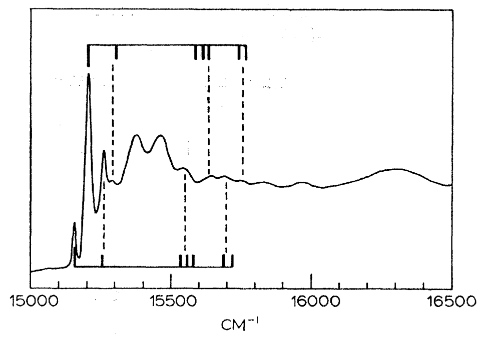

FIG. 8. Sideband positions expected in ZnO:Co, taking the doublets near 15 150 and 15 200 cm^{-1} in the axial spectrum as the no-phonon lines. Only phonons of zero wave vector are considered.

exactly, since the nickel concentration is not known, but the pair lines are an order of magnitude less intense than the single-ion lines.

5. DISCUSSION OF ZnO:Co RESULTS

The energy-level scheme of d^7 is more complex than that of d^8. In ZnO:Co, two multiplets, ^2G and ^4P, occur in the visible region, and transitions to all the levels from the G–$^4A_2(F)$ cubic field ground state are allowed.[6] Assignments are therefore more difficult than for ZnO:Ni.

The anisotropy of the spectrum indicates that a trigonal field is present. This splits the ground-state G level into two Kramers doublets,[27] an $E_{1/2}$ ground state and an $E_{3/2}$ state at 5.5 cm^{-1}. Transitions from both of these levels are seen in the optical spectra, verifying the ground-state splitting value. Pulsed-field Zeeman study of the very sharp lines[16] has been used to find the g values for the two components of the ground state and for the lowest level of the band, giving the assignment $E_{1/2}$—$^2E(e^4t_2^3)$ to the upper level for the sharp lines at 15 140 and 15 146 cm^{-1}. The temperature dependence[16] verifies that the splitting is a ground-state splitting. The line at 15 182 cm^{-1} in π polarization also shows by its temperature dependence that the lowest state of the transition is thermally populated. The integrated area of the line between 7 and 20°K gives a Boltzmann factor appropriate to absorption occurring from an energy level 5 cm^{-1} above the ground state. The line can therefore be identified as a transition to the same upper state as for the strong σ line at 15 189 cm^{-1}. Since the ground state is $E_{1/2}$ and the first excited state is $E_{3/2}$, the upper state is identified by polarization as an $E_{3/2}$. The line at 15 201 cm^{-1}, since it appears in π and σ, is a transition from the ground state to an $E_{1/2}$ level.

The weak lines due to transition-ion pairs show more structure than the corresponding lines of ZnO:Ni. The doublet structure apparent in the three sets of lines 15 070–15 078, 15 088–15 093, and 15 112–15 116 cm^{-1} fits the 5.5-cm^{-1} ground-state splitting of the single ion, but none of the components appear to show the temperature dependence characteristic of thermal population.

The spectral region above 15 200 cm^{-1}, as for ZnO:Ni, exhibits a different temperature dependence from the sharp lines, which suggests that lattice interaction is involved in this case also. Figure 8 shows the phonon sidebands to be expected from the $\mathbf{k}=0$ modes, taking 15 200 and 15 150 cm^{-1} as no-phonon line positions, and neglecting the splitting of each. It can be seen that there is a reasonable fit. As for ZnO:Ni, the 101-cm^{-1} mode seems to be present.

The two peaks at 15 370 and 15 460 cm^{-1} do not fit any sideband positions, so it may be assumed that they are associated with electronic transitions other than those of the sharp lines. The roughly Gaussian shape of the peaks suggests that the excited states are so distorted by electron-lattice interaction that the no-phonon lines are lost and only a multiphonon band is visible.[9]

6. JAHN-TELLER EFFECTS IN ZnO : Ni

The polarization of the π line at 15 208 cm^{-1} indicates that it is an A_1 level if the symmetry is trigonal. The energy difference from the strong E-level line shows that more is involved than a simple relaxation of selection rules. A shift due to different nickel isotopes[28,29] can be ruled out, since this could only split the σ polarized line into two main components in 2:1 ratio of intensity, but not transfer intensity to π polarization. Another possibility is the existence of more than one type of Ni^{2+} center, excluding next-nearest-neighbor interaction of transition ions. Any local effects due to the Ni^{2+} substitution in the lattice should produce only one type of center. Different sites could be produced by the presence of impurities, lattice vacancies or interstitials, but if such lattice defects were present in sufficient numbers to produce an appreciable effect on the Ni^{2+} spectra, the ZnO absorption edge would be considerably shifted by the perturbations to the electronic band structure.[30]

Assuming only one type of center, the lines cannot be explained on a static-field model. The twofold degenerate E level in $3m$ symmetry can be split into two levels by reduction of the local symmetry to m. One of these levels, labeled by A', the identity representation, should be observable on σ and π polarizations, while the other, A'', is allowed in σ only. This differs from experiment in that the 15 208-cm^{-1} level appears

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in π only. Also, the $A_1 \rightarrow A'$ level at 15 163 cm^{-1} does not appear in σ polarization as strongly as the 15 208-cm^{-1} line appears in π. Though not impossible, it seems unlikely that for both of these lines, the dipole matrix element for σ polarization should vanish for other than site symmetry reasons, when the lines appear in the π spectrum. The hypothesis that the two components of the trigonal E level are separated by a lower-symmetry field also disagrees with the observation of the splitting of the 15 200-cm^{-1} line into two components in the axial Zeeman spectrum. The twofold degeneracy shown by this verifies that the symmetry is in fact trigonal.

The dynamic Jahn-Teller effect, which has significant effects in the spectra of some transition ions in wurtzite structures,[9] is a possible explanation. An E electronic state can interact by electron-lattice coupling with local distortions whose symmetry is included in the sum $E \times E = A_1 + A_2 + E$. The interaction with A_1 and A_2 is trivial, but E distortions can give observable effects.[8] The coupling gives vibronic states of symmetry A_1, A_2, and E. Transitions from the A_1 ground state to the A_2 state are forbidden in trigonal symmetry, leaving the A_1 and E levels, which agrees with observation. Though the A_1 level is produced by vibrational interaction, its temperature dependence should at low temperatures be similar to that of the no-phonon lines, since only zero-point vibrations are involved. This again agrees with observation.

It should be emphasized that this apparent production of no-phonon lines not expected on the crystal-field model can occur only with E states. For T states in cubic symmetry the three basis electronic states may be split,[9] but no extra levels are produced. The two components of an E state are mixed with vibration functions, producing a series of levels.[8] In the present case, a cubic field T_2 state is split into an A_1 and an E state by a trigonal field, thereby making the Jahn-Teller splitting possible. If the trigonal field is small, as appears to be the case for ZnS:Ni, the Jahn-Teller produced A_1 level would not appear.

There is other evidence of vibrational effects in ZnO:Ni. The reduction of off-diagonal matrix elements of electronic operators by an overlap term for distorted electronic states, as discussed by Ham,[10] has been observed in ZnO:Cu,[9] CdS:Co,[9] and Fe^{2+} in some cubic crystals,[31] in the form of quenching of spin-orbit splitting. This brings spin-orbit components much closer together than expected with a static-field model. While there is insufficient spectral data in the visible band of ZnO:Ni to test this, the levels of $^3T_2(F)$ in the 4200-cm^{-1} region appear to require a very small spin-orbit parameter for fitting.[16] This indicates that Jahn-Teller interaction is occurring in the ^3F states, while the low g value found for the $E - T_2(^3P)$ line is evidence for interaction in the ^3P. Unexplained structure on no-phonon lines has also been found with Mn^{2+} in ZnS, ZnSe, and CdS,[17,18] so it appears that wurtzite-structure crystals are a suitable system for further study of these effects. In the Zn compounds particularly, the identification of lattice-phonon energies[17,31] suggests that local modes produced by the incorporation of $3d$ transition ions have only small effects, so that electron-lattice interaction is unimpeded by other large local perturbations.

7. CONCLUSION

The electron-lattice interaction appears to play a considerable part in determining the structure of the visible spectra of both ZnO:Co and ZnO:Ni. It appears desirable to identify as much of the phonon sideband structure as possible by the use of other techniques such as fluorescence. When no-phonon lines and sharp sideband components have been distinguished for both visible and infrared bands, quantitative calculation of Ham quenching parameters should be possible. This may resolve the difficulties at present associated with assignment of the spin-orbit parameter.[6,16] Further study of other systems may provide other examples of dynamic energy levels like the 15 208-cm^{-1} level of ZnO:Ni, to determine whether the Jahn-Teller effect is in fact responsible for the occurrence of additional no-phonon lines.

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