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The Electronic Structure of Lithium Metachromite[*]

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The single crystal absorption spectrum of $LiCrO_2$ has been measured at 300°, 80°, and 5°K. The spin allowed transitions ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}$ are observed at ~17 500 and ~24 000 cm^{-1}. The spin forbidden transitions ${}^4A_{2g} \rightarrow {}^2E_g$, ${}^4A_{2g} \rightarrow {}^2T_{1g}$ and ${}^4A_{2g} \rightarrow {}^2T_{2g}$ show an anomalous intensity vs. temperature dependence. This is attributed to an optical manifestation of the known antiferromagnetic behavior of $LiCrO_2$.

Introduction

Refractory systems in which it is possible to measure the single crystal electronic absorption spectrum of the Cr^{3+} ion undiluted by an isomorphous host are not common. This is due either to a lack of a band gap in the visible-uv or to such a high density of absorbing centers that it becomes physically impossible to grow crystals of sufficient thinness to obtain transmission of light. The spectrum of pure Cr_2O_3 (*1*) and pure $NaCrS_2$ (*2*) have been measured in their single crystal habit, however. To this group we wish to add our measurements on $LiCrO_2$.

Experimental

Single crystals of $LiCrO_2$ were prepared,[1] as hexagonal almost black platelets, by the method of Anderson and Schieber (*3*). These platelets have the (001) crystallographic face predominant and appear to be the only growth habit obtainable by this technique. $LiCrO_2$ belongs to a hexagonal space group, $R\bar{3}m$, (*4*) with the Cr^{3+} ions on sites of D_{3d} symmetry. This affords us the opportunity to measure only the axial spectrum. For this reason we were unable to collect polarization data.

Optical measurements were obtained at 300°, 80°, and 5°K by techniques previously described (*5–7*). A typical crystal measured 2 mm across and .04 mm thick. The area of an absorption band, with the ordinate in units of ϵ molar and abscissa, cm^{-1}, was estimated using a planimeter. The value thus obtained, $\int \epsilon d\nu$, was multiplied by 4.32×10^{-9} to yield a value of f, oscillator strength. The molar extinction coefficients and oscillator strengths, Table I, are probably correct only within ±5% due to inaccuracy in measurement of the thickness (±.005 mm) and inaccuracy of planimetric measurements.

TABLE I

Transition	T. (°K)	ν max (cm^{-1})	ϵ max	$f \times 10^6$
${}^4A_{2g} \rightarrow {}^2E_g$	80	14 250	.98	2.85
	5	14 250	1.82	4.27
${}^4A_{2g} \rightarrow {}^2T_{1g}$	80	14 850	1.73	5.95
	5	14 850	2.22	7.60
${}^4A_{2g} \rightarrow {}^4T_{2g}$	300	17 350	6.45	82.30
	80	17 500	5.20	50.60
	5	17 600	5.30	50.60
${}^4A_{2g} \rightarrow {}^2T_{2g}$	80	19 550	7.60	.38
	5	19 550	8.70	.78
${}^4A_{2g} \rightarrow {}^4T_{1g}$	5	23 750	10.85	200.00

Results and Discussion

Crystal field theory predicts three spin allowed transitions for Cr^{3+} in an octahedral field (*8, 9*). In order of increasing energy these are ${}^4A_{2g}$ to ${}^4T_{2g}$, ${}^4T_{1g}$ and ${}^4T_{1g}$ (P). The positions of these and the number and pattern of the less intense spin forbidden lines have been observed to be sensitive to site symmetry, (*10–12*) and anion (*1, 13*) and cation (*14*)

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[1] Crystals used in the initial phases of this investigation were supplied by A. Tauber.

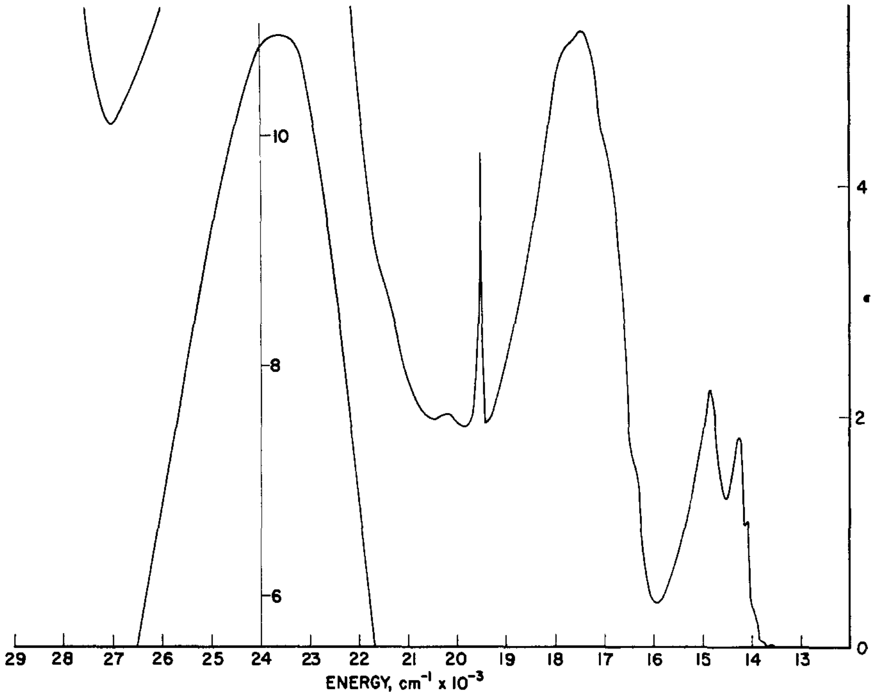

FIG. 1. The absorption spectrum of $LiCrO_2$ at 5°K.

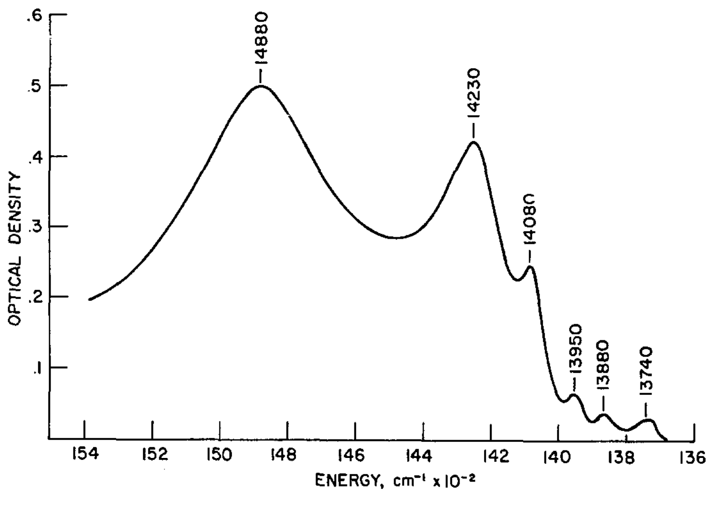

FIG. 2. The 5°K absorption spectrum of $LiCrO_2$ in the ^2E region.

covalency and size. Our assignments of the absorption bands in Figs. 1 and 2 as indicated in Table I are in agreement with relative positions calculated (*9*, *15*) and positions and oscillator strengths observed (*16*) for Cr^{3+} in nearly octahedral oxide lattices. The separation between the ^2E_g and $^2T_{1g}$ bands (600 cm^{-1}) is comparable to that observed in Cr_2O_3 (550 cm^{-1}) (*1*) and calculated for Cr^{3+}: MgO (570 ± 20 cm^{-1}) (*10*). The oscillator strengths, however, are ~10^2–10^3 times greater than those measured for the $^4A_{2g} \rightarrow {}^2E_g$ transition in chromium hexaquo complexes (*12*) and the intensities, relative to the $^4T_2$ maximum, appear to be comparable to those observed in Cr_2O_3 (*1*).

From the intensity and decrease in area of the $^4T_2$ band with decreasing temperature (Table I) it is reasonable to assume, at the onset, that the $^4A_2 \rightarrow {}^4T_2$ transition is essentially electric dipolar with a dynamic intensity giving mechanism. The intensity of the spin forbidden bands presumably comes about via spin–orbit coupling to this band. The oscillator strengths of the quartet-doublet transitions, however, increase with decreasing temperature. It is possible, therefore, that the intensity comes about by coupling to a portion of the $^4T_2$ band which arises from a nonzero magnetic–dipole transition moment or some electric–dipole transition modified by magnetic interactions which become prominent at low temperatures. Several considerations favor this conjecture. Significant magnetic–dipole character has been demonstrated for the $^4T_2$ (*12*) and ^2E (*17*) bands of Cr^{3+} in a cubic oxide host lattice. $LiCrO_2$ is antiferromagnetic (Tn = 200°K and $\theta = -550$°K). The coupling mechanism is believed to depend more upon interaction of the three t_{2g} electrons of Cr^{3+} with six nearest cationic neighbors than upon superexchange through the configurations M^{3+}–O–M^{3+} (*18*). The magnetic structure of the crystal at low temperatures, therefore, would be influenced by the ordinarily weak long-range interactions. That structural and magnetic changes can affect the electronic spectrum has been demonstrated in $KMnF_3$ (*19*). The mechanism of the acquisition of anomalous intensity of the spin forbidden transitions, in this molecule, was ascribed to both vibrationally perturbed electric–dipole and pure electronic (magnetic–dipole) transitions among spin-coupled ions with total spin of the exchange pair being conserved.

Substantial decrease in oscillator strength and shift of $\nu_{\max}$ (300–600 cm^{-1} toward the blue) with decreasing temperature from 300–4°K has been associated with a predominantly vibronic intensity giving mechanism (*20*, *11*, *2*). This sensitivity to temperature is absent or greatly diminished ($\Delta\nu_{\max}$ 60–100 cm^{-1}) when the band has significant magnetic–dipole character (*12*) or is influenced by magnetic changes (*19*). This type of behavior is observed in $LiCrO_2$ below 80°K, cf. Table I.

The fine structure revealed at 5°K (Fig. 2) near the ^2E_g band and on the $^4A_{2g}$ band, can be accounted for by contributions from vibrational modes and a small trigonal distortion. The number of components is correct but the separation too great for the shoulders on the $^4T_2$ band to correspond to the spin-orbit components, Γ_7, Γ_8, Γ_6 and Γ_8 as calculated for Cr^{3+}: MgO (*10*), Na_2KCrF_6 (*9*) and Cr^{3+}: Al_2O_3 (*14*). The $^4T_2$ band widths estimated in these calculations (100–450 cm^{-1}), however, are certainly too small (*10*, *11*). Therefore, although it is most reasonable, at present, to interpret the structure as part vibrational progression, it is worth remembering that longer-range lattice phenomena which are perhaps significant in this crystal at low temperature, are ignored in the crystal field calculation. Lattice vibrations have been observed at 200, 400, 500 and 600 cm^{-1} in spinel type chromites (*21*). Vibrations of $\nu \simeq 430$ cm^{-1} occur in both E_u and E_g modes of Al_2O_3. Corrected by the square root of the chromium-aluminum mass ratio assuming the vibration involves metal ion motion, this yields $\nu \cong 600$ cm^{-1}. A similar progression has been seen on the hexaquochromium $^4T_{2g}$ band (*12*). The vibronic coupling would involve the E_g mode if the transition were essentially magnetic dipolar (*23*).

The two peaks separated by ~300 cm^{-1} (Fig. 2) could arise from a vibration or trigonal distortion. Assuming the latter, a value of $|\nu|$, the first-order trigonal field parameter, is estimated to be ~600 cm^{-1} (*11*). A trigonal field of this strength would split the ^2E into a doublet separated by ~25 cm^{-1} ($\lambda = -4/3\ \zeta/[E(^2E) - E(^2T_2)]$ with $\zeta = 170$ cm^{-1}, $E(^2E)$ and $E(^2T_2)$ equal to 14 250 and 19 500 cm^{-1}, respectively, and $\nu = 600$ cm^{-1} (*12*). No such splitting of the ^2E band of $LiCrO_2$ was resolved at 4.2°K. The fine structure near the ^2E most probably arises from vibronic coupling with a frequency ~200 cm^{-1}. Fine structure of this magnitude has been observed in both dilute (*12*) and undiluted (*1*) Cr^{3+} cubic oxide crystals.

A value of the Racah parameter B was calculated to be 600 cm^{-1}, using the $^4T_1(^4P, {}^4F)$ energy matrix (*24*) and a value of 1750 cm^{-1} = D_q. The nephelauxetic ratio, $\beta = B/Bo$, with $Bo = 918$ cm^{-1} (*25*), is .660. These values are comparable within experimental error to those reported for other oxides.

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