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Absorption Spectra of $K_3Na(SO_4)_2$-Na_2CrO_4 and $LiKSO_4$-K_2CrO_4 Single Crystals[1]

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Absorption spectra of two mixed-crystal systems of chromate ion are reported. In one of these systems, $K_3Na(SO_4)_2$-Na_2CrO_4, the CrO_4^{2-} ion occupies a site of C_{3v} symmetry whereas in the other, $LiKSO_4$-K_2CrO_4, it occupies a C_3 site. Four absorption band systems are observed and are assigned, on the basis of polarization data, as follows: 4000 Å, $^1T_1 \leftarrow {}^1A_1$; 3600 Å, $^1T_2 \leftarrow {}^1A_1$; 2700 Å, $^1T_2 \leftarrow {}^1A_1$; 2400 Å, $^1T_1 \leftarrow {}^1A_1$.

Introduction

Many theoretical calculations have been carried out on the electronic structure of the T_d transition metal oxyanions.[2-7] Most of the experimental work has dealt with permanganate[8-15] with little information available for related systems.[16-18] The present investigation is concerned with the electronic spectrum of the chromate ion at helium temperatures. The systems chosen were $K_3Na(SO_4)_2$-Na_2CrO_4 and $LiKSO_4$-K_2CrO_4 mixed crystals.

These crystal systems were chosen for the following reasons. (i) The CrO_4^{2-} ion occupies a position of C_{3v} symmetry in the $K_3Na(SO_4)_2$ crystal and C_3 in the $LiKSO_4$ crystal.[19] These symmetry reductions ($T_d \rightarrow C_{3v}$ for the potassium-sodium salt and $T_d \rightarrow C_3$ for the lithium-potassium salt) should produce state splittings and allowedness-forbiddeness characteristics which might permit unique identifications for the states of the hypothetical parent tetrahedral molecule ion.

(ii) Both mixed-crystal systems are hexagonal. Consequently, polarization studies parallel ($\vec{E} \parallel \vec{C}$) and perpendicular ($\vec{E} \perp \vec{C}$) to the crystal *c* axis should refer to A ← A and E ← A transitions, respectively.

(iii) Both crystals are easily grown in virtually any desired host-guest concentration ratio.

Experimental Section

All chemicals were reagent grade. The sodium and potassium sulfates were obtained from J. T. Baker. The lithium sulfate was obtained from Fisher and the potassium chromate from Allied Chemical and Dye Corp. The sodium:potassium ratio chosen[20] in preparing the $K_3Na(SO_4)_2$ was 1.58. The lithium:potassium ratio chosen[20] in preparing the $LiKSO_4$ was 2.07. The crystals were grown from aqueous solutions. The chromate concentration in the sodium-potassium salt was 0.20 mol % and in the lithium-potassium salt was 3.5 mol %.

Spectroscopic measurements were made using a Cary 14 spectrophotometer in conjunction with both immersion and contact liquid-helium dewars. No appreciable differences were noted in the spectra obtained using either type of dewar. However, although the crystal temperature was found to be higher (*i.e.*, ~15°K) in the contact dewar, the inherent resolution was actually better because only two layers of quartz (instead of eight) intruded on the light path and allowed the use of smaller slit widths.

The nominal spectral bandwidths, based on slit width and instrumental dispersion factors, were as follows: 30 cm^{-1} at 25,000 cm^{-1}; 50 cm^{-1} at 30,000 cm^{-1}; 70 cm^{-1} at 35,000 cm^{-1}; 90 cm^{-1} at 40,000 cm^{-1}; 150 cm^{-1} at 45,000 cm^{-1}. The band maxima of sharp peaks were locatable with an uncertainty not larger than ±15 cm^{-1}.

Results

The absorption spectra obtained are shown in Figures 1 and 2. We describe here three absorption regions in detail (~ 3600, 2700, 2400 Å) and one other (~4000 Å) very briefly. In all cases, the $LiKSO_4$-K_2CrO_4 crystal cracked during the cooling from 77 to 4.2°K. This cracking, presumably caused by a phase change, greatly increased light-scattering effects. Therefore, all observations on $LiKSO_4$-K_2CrO_4 were restricted to 77°K.

Absorption Band Centered at 4000 Å. The vibrational analysis of the unpolarized spectrum is given in Table I. This lowest energy band has an apparent origin in the region of 21,500 cm^{-1}. It exhibits four weak but distinct vibrational peaks spaced by 807 cm^{-1}. The ~800-cm^{-1} vibrational interval common to this and all other resolved bands is the totally symmetric breathing frequency ν_1 (a_1) of the various excited states. The totally symmetric vibration has an average frequency of 847 cm^{-1} in the $^1A_1$ ground state.[21]

As is evident from Figure 2, this weak absorption band appears more intense in the ⊥-polarization spectrum for the C_{3v} system whereas it appears equally intense in both the ⊥- and ∥-polarization spectra of the C_3 system. Assuming these observations to reflect site effects, this lowest energy band must be assigned as an electric dipole forbidden $^1T_1 \leftarrow {}^1A_1$ transition of the parent tetrahedral ion. This assignment accords with the solidly based designation of the analogous "far-red" bands of permanganate ion.[14,15]

Absorption Band Centered at 3600 Å. The absorption spectra are shown in Figures 1 and 2. This absorption band appears comparably intense in both polarization directions regardless of whether the CrO_4^{2-} ion occupies a substitutional site of either C_{3v} or C_3 symmetry. In both cases, the spectra obtained in the ∥- and ⊥-polarization directions clearly represent electric dipole allowed transitions. The only electronic

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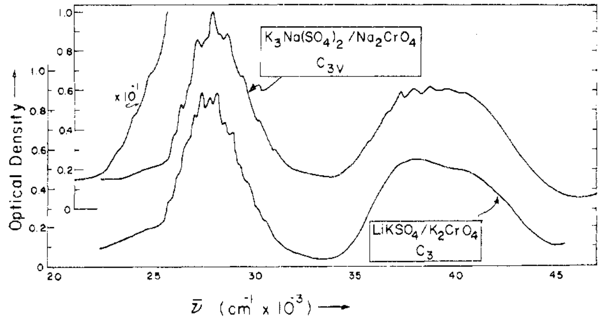

Figure 1. Absorption spectra of a single crystal of $K_3Na_2(SO_4)_2$-Na_2CrO_4 containing 0.2 mol % chromate salt at 4.2°K and of a single crystal of $LiKSO_4$-K_2CrO_4 containing 3.5 mol % chromate salt at 77°K. The outermost optical density scale refers to $LiKSO_4$-K_2CrO_4 and the innermost to $K_3Na(SO_4)_2$-Na_2CrO_4.

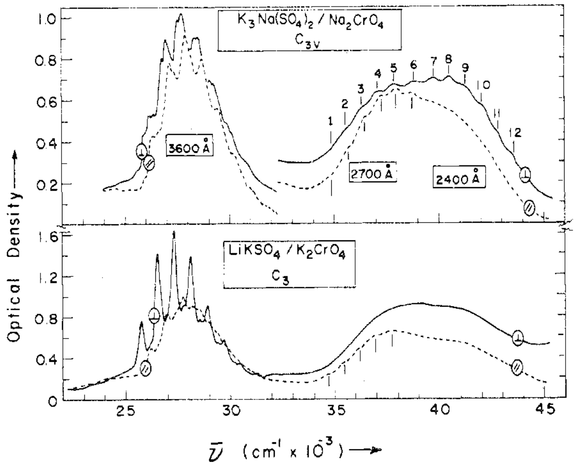

Figure 2. Polarized absorption spectra of the same two crystal systems studied in Figure 1. Absorption of light polarized parallel to the *c* axis is denoted by a dashed line; that polarized perpendicular to the *c* axis by a solid line. The band systems which are denoted in the text by names such as 4000-Å system, 3600-Å system, etc. are identified by the same names in this figure. Band systems in the 2700- and 2400-Å systems are labeled numerically for easy text reference.

Table I. Vibrational Structure in the Unpolarized 4000-Å Absorption Band of $K_3Na(SO_4)_2$-Na_2CrO_4

$\bar{\nu}$, cm^{-1}	$\Delta\bar{\nu}$, cm^{-1}	$\bar{\nu}$, cm^{-1}	$\Delta\bar{\nu}$, cm^{-1}
23,145		24,756	806
23,954	809	25,565	807
			Av 807

excitation of the CrO_4^{2-} ion consistent with the above results is $^1T_2 \leftarrow {}^1A_1$.

Vibrational analyses of the 3600-Å band system are given in Tables II and III. The analysis of the $LiKSO_4$-K_2CrO_4 crystal is particularly simple. As shown in Table III, it consists of progressions in the a_1 breathing mode built on a 26,205-cm^{-1} origin in the ‖ polarization and a 25,760-cm^{-1} origin in the ⊥ polarization. The weak vibrational substructure present in both spectra appears interpretable as a slight contamination of one polarization direction by the other. The crystal field splitting of the $^1A(\|)$ and $^1E(\perp)$ states is 555 cm^{-1}.

The 3600-Å band of the $K_3Na(SO_4)_2$-Na_2CrO_4 crystal exhibits what appears to be five independent origins, two of which appear in ‖ polarization and three in ⊥ polarization. An analysis of this system is given in Table II. The nature of the observed splitting within any given polarization direction is unknown to us. It may be of phonon or molecular vibrational nature, but the splittings appear too large for consistency with the former and too small for consistency with the latter of these interpretations. We are loath, in view of the perfection of the crystal systems chosen for viewing, to attribute these intense multiple origins to crystalline imperfections—yet, we must note the ability of $K_3Na(SO_4)_2$ to form solid solutions,[19] presumably randomized, with Na_2SO_4 and the possibility that sulfates and chromates of these types may do likewise. In other words, even though the multiple origins might be associable with CrO_4^{2-} defect sites of symmetry lower than C_3 or C_{3v}, we prefer either a mixed phonon vibrational point of view or a polarization "leakage" such as we believe is observed in $LiKSO_4$-K_2CrO_4. In any event, the spectrum is dominated by progressions in the a_1 breathing mode and, if we choose the most intense progressions in the ‖ and ⊥ polarizations (*i.e.*, the II and II′ progressions of Table II) as representative of the true C_{3v} site splitting, we find a 165-cm^{-1} separation of the $^1A(\|)$ and $^1E(\perp)$ states.

Table II. Vibrational Structure in the 3600-Å Absorption Band of $K_3Na(SO_4)_2$-Na_2CrO_4

System	Polarizn	$\bar{\nu}$, cm^{-1}	$\Delta\bar{\nu}$, cm^{-1}	Mode
I	Parallel	25,950	0	0,0
		26,660	710	ν_1
		27,360	705	$2\nu_1$
		28,080	710	$3\nu_1$
			Av 708	
II	Parallel	26,350	0	0,0
		27,130	780	ν_1
		27,890	770	$2\nu_1$
		28,680	777	$3\nu_1$
		29,430	770	$4\nu_1$
		30,210	772	$5\nu_1$
		31,000	775	$6\nu_1$
			Av 774	
I′	Perpendicular	25,975	0	0,0
		26,762	787	ν_1
		27,545	785	$2\nu_1$
		28,342	789	$3\nu_1$
		29,090	779	$4\nu_1$
		29,880	781	$5\nu_1$
			Av 784	
II′	Perpendicular	26,185	0	0,0
		26,955	770	ν_1
		27,740	778	$2\nu_1$
		28,530	782	$3\nu_1$
		29,260	769	$4\nu_1$
		30,105	784	$5\nu_1$
		30,880	783	$6\nu_1$
			Av 778	
III′	Perpendicular	26,375	0	0,0
		27,140	765	ν_1

Table III. Vibrational Structure of the 3600-Å Absorption Band of $LiKSO_4$-K_2CrO_4

Polarizn	$\bar{\nu}$, cm^{-1}	$\Delta\bar{\nu}$, cm^{-1}	Mode
Parallel	26,205	0	0,0
	26,983	778	ν_1
	27,755	775	$2\nu_1$
	28,490	762	$3\nu_1$
		Av 772	
Perpendicular	25,760	0	0,0
	26,546	786	ν_1
	27,345	792	$2\nu_1$
	28,129	790	$3\nu_1$
	28,927	791	$4\nu_1$
	29,700	788	$5\nu_1$
	30,469	784	$6\nu_1$
	31,328	795	$7\nu_1$
		Av 789	

Absorption Bands Centered at 2700 and 2400 Å. From the polarized spectra obtained for the $K_3Na(SO_4)_2$-Na_2CrO_4 crystal, the 2700-Å absorption band is seen to exhibit a weak vibrational structure in both polarizations. The parallel component is of slightly greater intensity and lies at higher energies. The site splitting estimated from 0,0 band positions is ~90 cm^{-1}. A vibrational analysis of this transition is given in Table IV. The dominant feature in both polarizations is a vibrational progression in the totally symmetric breathing mode. The totally symmetric vibration has an average frequency of 797 cm^{-1} in the $\parallel$ component and 778 cm^{-1} in the $\perp$ component. The only assignment of the 2700-Å band consistent with the experimental observations is a $^1T_2 \leftarrow {}^1A_1$ transition of the tetrahedral ion which splits into $^1A_1 \leftarrow {}^1A_1$ (parallel) and $^1E \leftarrow {}^1A_1$ (perpendicular) components in the C_{3v} site occupied in the $K_3Na(SO_4)_2$ matrix.

The average vibrational interval between the fifth and seventh peaks in the $\perp$ spectrum is 942 cm^{-1}. The seventh peak, therefore, is the origin (or pseudo-origin) of a second vibrational progression in the totally symmetric breathing mode with an average value of 767 cm^{-1}. A vibrational analysis of this $\perp$ component of the 2400-Å band is given in Table V. The existence of two absorption bands centered at 2700 and 2400 Å is, therefore, clearly indicated. The 2400-Å absorption band has a rather low intensity in the $\parallel$ spectrum and exhibits no vibrational structure. The assignment of the 2400-Å band which is most consistent with the experimental observations (*i.e.*, low intensity and no structure in the $\parallel$ polarization and considerable intensity and emergence of structure in the $\perp$ polarization) is a $^1T_1 \leftarrow {}^1A_1$ transition of the tetrahedral ion which splits into an allowed $^1E \leftarrow {}^1A_1$ (perpendicular) component and a forbidden $^1A_2 \leftarrow {}^1A_1$ component in the C_{3v} site occupied in the $K_3Na(SO_4)_2$ matrix.

From the polarized spectra obtained for the $LiKSO_4$-K_2CrO_4 crystal, the 2700-Å absorption band is seen to appear in both polarizations. A weak vibrational structuring is evident only in the less intense $\parallel$ spectrum. A vibrational analysis of this component is given in Table VI. The spectrum is dominated by a progression in the totally symmetric $\nu_1(a_1)$ mode.

A $^1T_2 \leftarrow {}^1A_1$ transition of the tetrahedral ion will split into $^1A \leftarrow {}^1A$ (parallel) and $^1E \leftarrow {}^1A$ (perpendicular) components in the C_3 site occupied in the $LiKSO_4$ matrix. This datum together with that for the sodium-potassium salt clearly substantiates the $^1T_2 \leftarrow {}^1A_1$ assignment of the 2700-Å band for the parent tetrahedral ion.

The 2400-Å absorption band also appears in both polarizations as is evident from Figure 2. No vibrational structure is present in either polarization. The absorption intensity is slightly greater in the $\parallel$ spectrum (after subtraction of residual intensity from the 2700-Å absorption band) whereas the $\perp$ component was more strongly absorbing in the case of the sodium-potassium salt. These data accord with $^1A \leftarrow {}^1A$ (parallel) and $^1E \leftarrow {}^1A$ (perpendicular) components of a split $^1T_1 \leftarrow {}^1A_1$ transition of the parent tetrahedral ion and with prior studies on the permanganate ion.[12]

Comments

The most important content of this work is the demonstration that the 2700-2400-Å absorption region consists of two electronic transitions and that these, in order of increasing energy, are of probable $^1T_2 \leftarrow {}^1A_1$ and $^1T_1 \leftarrow {}^1A_1$ types.

Table IV. Vibrational Structure in the 2700-Å Absorption Band of $K_3Na(SO_4)_2$-Na_2CrO_4

Polarizn	$\bar{\nu}$, cm^{-1}	$\Delta\bar{\nu}$, cm^{-1}	Mode
Parallel	34,875	0	0,0
	35,682	807	ν_1
	36,500	813	$2\nu_1$
	37,306	810	$3\nu_1$
	37,998	781	$4\nu_1$
	38,747	775	$5\nu_1$
		Av 797	
Perpendicular	34,785	0	0,0
	35,565	780	ν_1
	36,340	778	$2\nu_1$
	37,120	778	$3\nu_1$
	37,885	775	$4\nu_1$
		Av 778	

Table V. Vibrational Structure of the 2400-Å Absorption Band of $K_3Na(SO_4)_2$-Na_2CrO_4 (Perpendicular Polarization)

$\bar{\nu}$, cm^{-1}	$\Delta\bar{\nu}$, cm^{-1}	Mode[a]	$\bar{\nu}$, cm^{-1}	$\Delta\bar{\nu}$, cm^{-1}	Mode[a]
39,768	0	$n\nu_1$	42,068	767	$(n + 3)\nu_1$
40,530	762	$(n + 1)\nu_1$	42,850	771	$(n + 4)\nu_1$
41,300	766	$(n + 2)\nu_1$		Av 767	

[a] The zero-phonon line is occluded in this spectrum. Consequently, n may equal 1, 2, or 3.

Table VI. Vibrational Structure of the 2400-Å Absorption Band of $LiKSO_4$-K_2CrO_4 (Parallel Polarization)

$\bar{\nu}$, cm^{-1}	$\Delta\bar{\nu}$, cm^{-1}	Mode	$\bar{\nu}$, cm^{-1}	$\Delta\bar{\nu}$, cm^{-1}	Mode
34,674	0	0,0	36,941	756	$3\nu_1$
35,436	762	ν_1	37,764	773	$4\nu_1$
36,193	760	$2\nu_1$		Av 763	

Thus, these two transitions apparently occur in a reversed energy order in CrO_4^{2-} relative to the corresponding transitions in MnO_4^-.

That the 3600-Å system is of $^1T_2 \leftarrow {}^1A_1$ type is obvious simply on the basis of intensity considerations. The polarization results presented here agree on this. It is important to point out, however, that the structural details of this band system are not understood, as witness the dilemma of the five progressions of Table II. Similar difficulties have been encountered in the corresponding $^1T_2 \leftarrow {}^1A_1$ transition of MnO_4^- ion.[12-14] It seems clear that further work on this band system is in order.

The data presented here on the 4000-Å system of CrO_4^{2-} are, for a number of reasons, merely indicative. First, the resolution used may well have been inadequate to detect the very sharp low-intensity origin bands of this so-called Teltow absorption region[22] and, second, the observed absorptivity may refer only to the diffuse part of the Teltow absorption region.[22] Since this diffuseness is also present in the corresponding MnO_4^- Teltow band and is not understood,[14] it is difficult to be assertive about the meaning of the results obtained in this present work for the 4000-Å CrO_4^{2-} band.

Registry No. $K_3Na(SO_4)_2$, 16349-83-0; Na_2CrO_4, 7775-11-3; $LiKSO_4$, 14520-76-4; K_2CrO_4, 7789-00-6.

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