The Vibrational Spectra of Strontium Chromate (SrCrO₄) and Lead Chromate (PbCrO₄)

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The Raman spectra of the monoclinic compounds strontium chromate, lead chromate and of the mineral crocoite (PbCrO₄) have been recorded at 300 °K and 77 °K. The spectrum of the orthorhombic modification of lead chromate has also been recorded. The spectra of the monoclinic and of the orthorhombic PbCrO₄ were found to be indistinguishable, whereas the spectra of the isomorphous monoclinic salts SrCrO₄ and PbCrO₄ are remarkably different. Inversion doubling was observed in SrCrO₄ but less distinctly in monocristalline crocoite.

I. Introduction

SrCrO₄ and PbCrO₄ were investigated as a part of a comprehensive study of the Raman effect in inorganic chromates and dichromates. The particular interest in these substances is in an attempt to shed some light on the influence of the crystal field on the vibrational spectra of anions. It is known that monoclinic¹ SrCrO₄ and PbCrO₄ have almost identical unit cell dimensions. PbCrO₄ exists also in an orthorhombic² modification. No detailed analysis has thus far been undertaken to study the influence of phase transition and isomorphism of chromates by means of the Raman effect.

II. Experimental

1. Apparatus

Raman spectra were recorded on a photoelectrically recording spectrometer described elsewhere⁵ ⁴. Wave numbers quoted in this paper are accurate to within ±2 cm⁻¹.

For the low temperature work two types of cryostats were used. The first type was a conventional cryostat as used in IR transmission work adapted for 90⁰ scattering experiments by means of a copper cold finger protruding horizontally from the cryostat. A cylindrical Pyrex tube covers the cold finger. This cryostat was used for SrCrO₄ only. The lowest temperature which could be reached with liquid nitrogen as coolant and with the thermocouple embedded in the sample was 110 °K. Since the sample is kept under vacuum and cooled by conduction only, decomposition of PbCrO₄ by the focussed laser beam (λ = 6328 Å, P = 180 mW) could not be prevented.

The second type of cryostat simply consists of one Pyrex tube (150 mm x 10 mm i. d.) surrounded by another (100 mm x 20 mm o. d.). The space between the tubes, when properly evacuated, serves as a thermal insulation. The sample is put into the centre of the inner tube. Liquid nitrogen is fed into the inner Pyrex tube. A thermocouple pushed in from the other side is used to monitor the temperature. This double-walled Pyrex cryostat has two advantages. Firstly, liquid nitrogen temperature is easily reached and any temperature between 300 °K and 77 °K can be obtained by controlling the N₂ gas flow. Secondly, the sample is cooled by convection at the actual scattering area, so that any heating effect of the absorbed laser radiation is minimised. In the case of PbCrO₄ no decomposition occurs at 77 °K and 160 mW of focussed laser power (power density approximately 10⁴ W/cm²).

2. Sample Preparation

Strontium chromate was prepared by precipitation from aqueous solutions of Merck extra pure potassium chromate and Analar reagent strontium chloride, and dried at 200 °C. The X-ray powder pattern of this material was taken and found to be consistent with the one given by Pistorius¹. Monoclinic lead chromate was prepared by precipitation from aqueous solutions of Merck extra pure potassium chromate and Merck extra pure lead acetate, and dried at 200 °C. The X-ray powder pattern of this compound also was found to be consistent with the one given by Pistorius¹.

Lead chromate in its orthorhombic modification was prepared by precipitation from aqueous solutions of

¹ C. W. F. T. PISTORIUS and M. C. PISTORIUS, Z. Krist. 117, 4 [1962].
² G. COLLOTTI, L. CONTI, and M. ZOCCHI, Acta Cryst. 12, 416 [1959].

Merck extra pure potassium chromate and Merck extra pure lead nitrate and dried at 25 °C in vacuum. The X-ray powder pattern was found to be consistent with the one given by Collotti, Conti, and Zocchi.

The samples of crocoite of approx. 1×1×4 mm³ were of Tasmanian origin.

### III. Crystal Structure of SrCrO₄ and PbCrO₄

Space groups and unit cells of SrCrO₄ and the two modifications of PbCrO₄ are given in Table 1. The structure of SrCrO₄ has not been determined yet although Bragg and Clarringbull predicted SrCrO₄ to fall in the barite group which is orthorhombic with space group Pnma — D₄h, Z = 4. The structure of the mineral crocoite (PbCrO₄) has been established.

Brodys could, for crocoite, only determine the positions of the lead and chromium atoms while Quareni and De Pieri managed to determine the positions of the oxygen atoms and later presented refined data. The structure is as follows. The chromium atom is surrounded by an approximate tetrahedron of oxygen atoms at an average distance of 1.65 Å with bond angles varying from 105.7° to 113.1°. The lead atom is surrounded by seven CrO₄ tetrahedra, with Pb–Cr distances in the range 3.32 Å to 4.15 Å. The lead atom is also surrounded by ten oxygen atoms with Pb–O distances ranging from 2.53 to 3.44 Å; all the other Pb–O distances are greater than 4.03 Å.

The structure of orthorhombic lead chromate PbCrO₄ has also been worked out.

The positions of the atoms were calculated by means of a method based on trial and error. This was done under the assumption of regular CrO₄ tetrahedra. It will be shown in this work that the tetrahedra in SrCrO₄ and both modifications of PbCrO₄ are in fact distorted.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Ref.</th>
<th>System</th>
<th>Space group</th>
<th>Z</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrCrO₄</td>
<td>1</td>
<td>monoclinic</td>
<td>P₂₁/n — Cs₂</td>
<td>4</td>
<td>7.081</td>
<td>7.388</td>
<td>6.771 Å ± 0.01 Å</td>
<td>103°25'±5'</td>
</tr>
<tr>
<td>PbCrO₄</td>
<td>1</td>
<td>monoclinic</td>
<td>P₂₁/n — Cs₂</td>
<td>4</td>
<td>7.118</td>
<td>7.434</td>
<td>6.794 Å ± 0.004 Å</td>
<td>102°25'±2'</td>
</tr>
<tr>
<td>crocoite</td>
<td>7</td>
<td>monoclinic</td>
<td>P₂₁/n — Cs₂</td>
<td>4</td>
<td>7.12</td>
<td>7.43</td>
<td>6.79 Å</td>
<td>102°25'</td>
</tr>
<tr>
<td>PbCrO₄</td>
<td>2</td>
<td>orthorhombic</td>
<td>Pnma — D₄h</td>
<td>4</td>
<td>8.67</td>
<td>5.99</td>
<td>7.13 Å ± 0.02 Å</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Space groups and unit cells of SrCrO₄ and PbCrO₄.

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The structure of synthetic monoclinic PbCrO₄ remains to be determined.

### IV. Results and Discussion

#### 1. Strontium Chromate

The Raman spectra of strontium chromate at 300 °K and 110 °K were obtained by focussing the laser beam on the powder pellet at an angle of approximately 45° and observing the scattered light perpendicular to the incident beam. Results are listed in Table 2 together with the Raman data of Griffith. The infrared data are taken from Afremow and Vandeberg. The low temperature Raman spectrum is shown in Fig. 1.

A regular CrO₄ tetrahedron possesses T₄ symmetry. The optically active vibrations are v₁: A₁(R), v₂: E(R), v₃: F₂(R, IR), v₄: F₃(R, IR). Neglecting the observed splitting in the first instance, it appears that the spectra can only be explained under the assumption of lifted degeneracies due to a distorted tetrahedron since 7 IR bands and 9 Raman bands have been observed. The total number of 9 Raman bands fits perfectly with the allowed number of vibrations for a five-atomic ion. However, 6 of these are split by 5 to 13 cm⁻¹ in the Raman and 2 bands are split by 10 and 12 cm⁻¹ in the IR. There is a strong indication that the observed splitting is due to inversion doubling of two coupled CrO₄ ions since the splitting of the Raman bands is smaller than that of the corresponding IR bands as demanded by theory, viz.,

- R(857/866 cm⁻¹), Δν = 9 cm⁻¹,
- IR(845/855 cm⁻¹), Δν = 10 cm⁻¹,
- R(889/893 cm⁻¹), Δν = 4 cm⁻¹,
- IR(875/887 cm⁻¹), Δν = 12 cm⁻¹.

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Table 2. Vibrational data of SrCrO$_4$.

<table>
<thead>
<tr>
<th>$\nu$</th>
<th>$I$</th>
<th>$\nu$</th>
<th>$I$</th>
<th>Raman</th>
<th>Slit:</th>
</tr>
</thead>
<tbody>
<tr>
<td>[cm$^{-1}$]</td>
<td></td>
<td>[cm$^{-1}$]</td>
<td></td>
<td>[cm$^{-1}$]</td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>vw b</td>
<td>344 (2)</td>
<td>354 (3)</td>
<td>366</td>
<td>116</td>
</tr>
<tr>
<td>380</td>
<td>407 (6)</td>
<td>373</td>
<td>146</td>
<td>12.2</td>
<td>401</td>
</tr>
<tr>
<td>431</td>
<td>w sp</td>
<td>437 (2)</td>
<td>432</td>
<td>14</td>
<td>6.6</td>
</tr>
<tr>
<td>845</td>
<td>s sp</td>
<td>864 (5)</td>
<td>857</td>
<td>555</td>
<td>5.5</td>
</tr>
<tr>
<td>875</td>
<td>vw sp sh</td>
<td>870 (10)</td>
<td>896</td>
<td>1030</td>
<td>4.9</td>
</tr>
<tr>
<td>887</td>
<td>s sp</td>
<td>898 (9)</td>
<td>893</td>
<td>850</td>
<td>4.4</td>
</tr>
<tr>
<td>912</td>
<td>s m</td>
<td>915</td>
<td>180</td>
<td>4.9</td>
<td>920</td>
</tr>
<tr>
<td>927</td>
<td>s sp</td>
<td>928</td>
<td>70</td>
<td>4.7</td>
<td>934</td>
</tr>
</tbody>
</table>

$I$ Intensities are peak values in arbitrary units, cannot be transferred from one spectrum to another and are not corrected for spectral response.  $d$ doublet.

It is reasonable to assume that the strongest band in the Raman spectrum (860/867 cm$^{-1}$ doublet) is the totally symmetric $A_t$ vibration. The splitting of this band cannot be explained by means of factor group analysis as can be seen from Fig. 2 where the correlation diagram for the possible site symmetry $C_2$ is shown.

The other phonons observed in the region between 892 and 934 cm$^{-1}$ must originate from the triply degenerate $r_3(F_2)$ vibration. One component was found split (892/897 cm$^{-1}$ doublet), the others are single.

The wave number region 337 to 436 cm$^{-1}$ contains the phonons originating from the $r_2(E)$ and
Another explanation for the observed splittings could be given if two crystallographically and energetically distinct \( \text{CrO}_4^{2-} \) ions are present in the lattice, giving rise to distinct vibrations. The rule of mutual exclusion would then not be applicable and corresponding bands should occur at the same energies in the infrared and Raman spectra. It can be seen by inspecting Table 2 that this is clearly not the case.

Judging from the vibrational data, it would appear that the structure of \( \text{SrCrO}_4 \) contains distorted \( \text{CrO}_4^{2-} \) tetrahedra (symmetry \( C_2 \) or \( C_2^\alpha \)) with the Cr atoms in general positions related pairwise by a center of symmetry.

2. Lead Chromate

2.1. Synthetic Lead Chromate

Raman spectra at 300 °K and 77 °K of the monoclinic and at 77 °K of the orthorhombic modification were obtained in the same manner as in the case of \( \text{SrCrO}_4 \). The results are listed in Table 3 and the low temperature spectrum is shown in Fig. 3.

Although monoclinic strontium and lead chromates belong to the same space group and possess...
almost identical unit cells, their vibrational spectra are quite different. On the other hand, the spectra of monoclinic crocoite, monoclinic synthetic lead chromate and orthorhombic synthetic lead chromate are almost indistinguishable. The only significant difference in the Raman spectra of monoclinic and orthorhombic lead chromate lies in the scattering efficiency. The bands of the monoclinic form are approximately eight times as intense as those of the orthorhombic form. This can partly be due to the influence of different particle size in the sample.

The total number of 12 bands in the R and of 5 bands in the IR spectra suggests again that the \( \text{CrO}_4^{2-} \) ion is a distorted tetrahedron causing all degeneracies to be lifted.

2.2. Crocoite, \( \text{PbCrO}_4 \)

Single crystal Raman spectra of this mineral were taken at 300 °K and 77 °K. In order to obtain meaningful results\(^{11} \) from a monoclinic crystal with an extraordinary high birefringence (\( N_x = 2.31 \text{ Li}, N_y = 2.37, N_z = 2.66; \) optic plane: 010; \( Z \perp c = -5.5^\circ \))\(^{12} \), it is necessary to choose an arrangement where neither the incident nor the scattered radiation becomes depolarized. Therefore, the crocoite specimen was cut normal to the \( c \) axis and polished to 1 mm thickness. The crystal was then examined in transmission with the incident and scattered radiation parallel to the \( c \) axis. This setup was checked by determining the depolarization ratio of the Rayleigh line; it was found to be \( \psi = 0.01 \), with the collecting lens set at 1 : 4 aperture for this and all the single crystal measurements.

The results of these single crystal measurements are listed in Table 4 together with the assignments. The first column gives the wave number of the observed bands, the following four columns give the relative intensities and half width in four meaningful scattering-configurations. The symbol \( c(b \perp b) \) indicates\(^{13} \) that the incident and scattered radiation propagate along the \( c \) axis, the incident radiation being polarized parallel to the \( b \) axis and the scattered radiation being analysed normal to the \( b \) axis. It should be noted that the direction \( b \perp b \) is not coincident with the \( a \) axis.

The significance of the low temperature single crystal spectrum can be seen in the excellent resol-
tion obtained, especially in the region from 820 to 883 cm\(^{-1}\). At 300 °K all bands marked sh had to be deduced from their envelopes by graphical methods. The intensities and half width of these bands are, therefore, subject to a larger error.

Considering the Raman tensor of the monoclinic class 2/m - C\(_{2h}\) given by Loudon\(^{14}\) the assignment of most of the bands is straightforward. Only a few bands show mixed A\(_g\) + B\(_g\) character.

The connection of the assignment obtained from single crystal measurements with the vibrations of the distorted tetrahedron is done on the basis of the T\(_{d}\) point group. The most intense band in the 820 to 883 cm\(^{-1}\) region is assigned to the \(v_1(A_1)\) stretching vibration. The only other vibration which can be possibly active in this region is the \(v_3(F_2)\) bending vibration which is triply degenerate. In order to account for the observed three \(A_g\) and three \(B_g\) phonons, it must be concluded that the degeneracy of the \(v_3(F_2)\) vibration is lifted and that each component is split into an \(A_g\) and \(B_g\) component.

In the region from 325 to 401 cm\(^{-1}\) the doubly degenerate \(v_2(E)\) bending and the triply degenerate \(v_4(F_2)\) bending vibration can be expected. Since nine phonons are observed, if the three bands showing mixed character are counted as six separate phonons, the assignment follows the same pattern as above. All degeneracies are lifted and each component appears split into \(A_g\) and \(B_g\). One \(B_g\) phonon remains unobserved. The division of the observed phonons into a group originating from \(E\) and \(F_2\) vibrations, respectively, can only be made tentatively under the assumption that the \(E\) vibration is of lower energy than the \(F_2\) vibration.

### 3. Inter-ionic Forces

It is interesting to note that the wave number of the totally symmetric stretching vibration \(v_1(A_1)\) is significantly lower in PbCrO\(_4\) (840 cm\(^{-1}\)) than in SrCrO\(_4\) (860/867 cm\(^{-1}\)). The weakening of the chromium-oxygen bond can be understood under the assumption of a strengthened lead-oxygen bond which means that the character of the lead-oxygen bond has become partly covalent.

If one allows the insolubility of a chromate to be considered as a measure of bond strength between cation and anion, the conclusion may follow that for the chromate with the highest solubility the wave number of \(v_1(A_1)\) is also highest and the character of the cation-anion bond has greater ionic character.

In Table 5 wave numbers of vibrations \(v_1(A_1)\) are listed for a number of Chromates, together with the solubilities of these compounds in water\(^{15}\).

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\(^{15}\) Handbook of Chemistry and Physics, 40th ed., Chemical Rubber Publishing Co., Cleveland, Ohio 1958.
**Partielle Interferenz- und partielle Atomverteilungsfunktionen**

sowie elektrischer Widerstand von geschmolzenen Magnesium—Zinn-Legierungen *

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From measured intensity functions, published in a previous paper, partial interference functions, partial pair correlation functions, partial atomic distribution functions, and partial coordination numbers were calculated and discussed. According to the theory of Faber and Ziman, the electrical resistivity of molten Mg—Sn alloys was calculated from the partial interference functions and from pseudopotentials reported by Animalu and Heine. The calculated values, being normalized to the resistivity of the molten components, are in good agreement with values measured by a rotating field method.

The partial interference functions are derived by the assumption of independency of concentration. This assumption is proved by discussion of the partial coordination numbers and the results of electrical resistivity determinations.

Für die Berechnungen des elektrischen Widerstandes geschmolzener Legierungen aus Röntgen-Beugungsdaten nach Faber und Ziman ¹ ist neben der Kenntnis der Pseudopotentiale ² die der partiel- len Interferenzfunktionen notwendig. Die partiel- len Interferenzfunktionen wurden bisher für die Systeme Cu-Sn ³, Ag-Mg ⁴, sowie Au-Sn und Ag-Sn ⁵—⁷ angegeben. In vorliegender Arbeit werden die partiel- len Interferenzfunktionen für das System Mg-Sn aus

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<table>
<thead>
<tr>
<th>CaCrO₄·2H₂O</th>
<th>SrCrO₄</th>
<th>BaCrO₄</th>
<th>PbCrO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1(A_1)$ at 300 K</td>
<td>880</td>
<td>857/866</td>
<td>863</td>
</tr>
<tr>
<td>solubility [g/100 ml] at °C</td>
<td>22.4°</td>
<td>0.12 15</td>
<td>0.00034 16</td>
</tr>
</tbody>
</table>

Table 5. Wave number of $v_1(A_1)$ versus solubility at °C for various chromates.

It can also be argued that the deviation ¹⁶ of the Cr—O—Cr bond angle from the ideal value 109.5° observed in crocoite originates from a strengthened Pb—O bond thus causing a decreased bonding power of the narrow tetrahedral $d^3$ orbitals of chromium. This, in turn, would lead to a decrease in the $v(A_1)$ frequency as observed.

Acknowledgements

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