THERMODYNAMIC AND SPECTROSCOPIC PROPERTIES AND LOW TEMPERATURE THERMOCHROMISM OF CHROMIUM TRIS–ACETYLACETONATE

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Abstract

Two narrow anomalies with peaks at $\sim 30\,K$ and $\sim 60\,K$ and a wide diffuse anomaly within the range $110 - 240\,K$ have been found in a low temperature heat capacity of chromium tris–acetylacetonate $Cr(AA)_3$. Besides, the reversible change in color has been discovered when cooling the crystals to liquid nitrogen temperature (thermochromism). To clear up the nature of these effects the static magnetic susceptibility was measured within the temperature range $2 - 300\,K$, the ESR–spectra on the $Cr^{3+}$ ion and the transmission spectra in visible region were recorded at $78\,K$ and $300\,K$, the Raman spectra were measured within the range $5 - 220\,K$. It has been ascertained that the reversible effect of thermochromism is observed in most of $\beta$–diketonates of the transition metals. Some tentative considerations concerning the origin of discovered effects are put forward.
1 Introduction

The chromium tris–acetylacetonate $\text{Cr}(C_5H_7O_2)_3$ (or $\text{Cr}(\text{AA})_3$) belongs to the $\beta$–diketonate complexes of transition metals crystallizing in the molecular type lattices. The $\beta$–diketonates of metals $\text{Me}(\text{AA})_3$ are widely used in practice (to separate metals, to apply metal coatings, as catalysts etc.). The field of their application is extending with time, which encourages their further comprehensive investigations. The compounds $\text{Me}(\text{AA})_3$ were actively studied in thermodynamical [1–3] and crystallochemical [4] aspects. In the recent years they have became the subject of theoretical inquiry [5, 6].

When investigating the properties of $\beta$–diketonates we have found some interesting effects in these compounds, before unknown. In this work two of such effects have been detected in the properties of $\text{Cr}(\text{AA})_3$: 1) anomalies in low temperature heat capacity; 2) a reversible change in color of crystals when cooling them to liquid nitrogen temperature (thermochromism).

2 Experimental

The samples $\text{Cr}(C_5H_7O_2)_3$ synthesized for this investigation are crystalline powder with the average size of crystallites 0.3–0.5 mm. At the room temperature they are dark violet. The samples were defined by the methods of chemical analysis, IR–spectroscopy, derivatography and X–ray phase analysis.

The heat capacity of $\text{Cr}(\text{AA})_3$ has been measured by the adiabatic method within the range $5 - 320 \, \text{K}$ using the installation described in Refs [7, 8]. The anomalous component was extracted by subtracting the regular heat capacity obtained by means of technique described in [9, 10]. Three anomaly were found in the heat capacity: the small peak at $\sim 30 \, \text{K}$, the anomaly with maximum at $\sim 60 \, \text{K}$, and the broad anomaly within the range $110 - 240 \, \text{K}$ (see Fig. [1]).

![Figure 1: Anomalous component of heat capacity $\delta C(T)$ of $\text{Cr}(\text{AA})_3$.](image-url)
The anomalies in maxima are correspondingly 0.9%, 3.2% and 0.3% of a regular heat capacity. The corresponding contributions to the entropy are: \( \Delta S \simeq 0.07J \text{ mol}^{-1}K^{-1} (30 \text{ K}) \), \( \Delta S = 1.20 \pm 0.05J \text{ mol}^{-1}K^{-1} (60 \text{ K}) \) and \( \Delta S = 1.5 \pm 0.25J \text{ mol}^{-1}K^{-1} \) (the broad anomaly).

To understand the nature of found anomalies we have measured the static magnetic susceptibility, the Raman spectra, the ESR–spectra on the ion \( Cr^{3+} \), the transmission spectra in visible region and have followed the change in color with temperature.

The static magnetic susceptibility of \( Cr(AA)_3 \) was measured by MPMS–5s SQUID–magnitometer (of Quantum Design) within the temperature range 2–300 K (Fig. 2). The obtained data showed the experimental points to fit in well with the Curie–Weiss low. No pronounced magnetic anomalies were observed. But at the attentive consideration one could see a weak deviation of experimental points from the Curie–Weiss low within the temperature range 140 – 190 K.

The ESR–spectra on the ion \( Cr^{3+} \) in \( Cr(AA)_3 \) single crystals were recorded using E – 109 Varian spectrometer at the frequency 9.5 GHz and at the temperatures 300 K and 78 K (Fig. 3). The ground orbital state of \( Cr^{3+} \) ion in the octahedral surrounding of \( Cr(AA)_3 \) is singlet; \( g \)–factor of 3\( d^3 \) configuration of ion \( Cr^{3+} \) is close to \( g = 2 \) \[1\]. The large anisotropy of ESR–spectra has been observed which results from large shifts of spectra due to the large second order corrections to the parameters of fine structure when the initial split is comparable with Zeeman interaction. The decrease of temperature from 300K to 78 K results in the broadening of lines without any change of their positions, for some lines such a broadening results in their total disappearance.

The transmission spectra of \( Cr(AA)_3 \) within the frequency range 11000 – 30000 cm\(^{-1} \) have been obtained at room and nitrogen temperatures using the two–ray spectrophotometer Specord of UV – 200 type (Fig. 4). The sample was prepared of powder placed between two quartz plates and then heated up to \( Cr(AA)_3 \) melting temperature (489 K). After cooling the solid continuous layer of \( \sim 0.01 \text{ mm} \) thick was formed.

Comparing the spectra obtained in the green region (18100 cm\(^{-1} \)) at room and nitrogen temperatures one can see the shift of the transmission band maximum to the violet side by

![Figure 2: Magnetic susceptibility \( \chi \) as a function of temperature for \( Cr(AA)_3 \).](image)

\( 1/\chi = (T+0.56)/1.831 \)
600 cm$^{-1}$. This shift exceeds the expected shift resulting from the temperature expansion of crystal lattice.

The Raman spectra of $Cr(AA)_3$ (Fig. 5) were recorded with a Triplemate, SPEX spectrometer equipped with a O–SMA, Si–diode array. The 633 nm, 50 mW line of an $He-Ne$–laser was used for the spectral excitation. For the low temperature measurements the sample was fixed on a cold finger of the helium cryostat (APD Cryogenic Inc). The measurements were carried out within the temperature range $5 - 220 K$. The temperature was established within the accuracy of 0.1 K.

The frequency interval 40 – 100 cm$^{-1}$ is the range of crystal lattice vibrations. The interval 100 – 150 cm$^{-1}$ is the borderline range of the lattice and molecular vibrations. The higher frequencies are rated as molecular ones. The band within the range 40 – 100 cm$^{-1}$ being wide at 220 K splits up into the separate components when the temperature decreases. The detail analysis showed that the frequencies of these components depend on the temperature, but their relative intensity doesn’t depend on it. When the temperature reaches $\sim 60 K$ the new band at 109 cm$^{-1}$ appears which was absent at higher temperature.

It was discovered in this work that the sample dark–violet at the room temperature becomes red when immersed into liquid nitrogen (thermochromism). This change in color is reversible. In order to follow the change in color with temperature, a special experiment was carried out. The sample placed on a copper substrate was immersed in the bath with liquid nitrogen. Temperature of the substrate and sample was measured by copper–constantan thermocouple, the color of the sample was estimated by eye. When the temperature slowly increased, the red color had remained within the range 78 – 120 K. The color of the sample varied smoothly within the range 120 – 210 K, at 210 K it had turned dark violet and then it stayed as such at the further increase of temperature up to room one.

An additional experiment with 36 compounds showed that the reversible effects of thermochromism was observed for most of $\beta$–diketonates of transition metals, when cooling them with the liquid nitrogen. Most of tried 36 compounds grew light when the
(III), copper (II) and chromium (III) compounds. The compound Co(AA)$_3$, being dark green at room temperature, became violet. The compound Cu(AA)(hfa)–copper(II) acetylacetonate – hexafluoroacetylacetonate, being green at room temperature, became blue. The change in color of Cr(AA)$_3$ has been described above.

3 Discussion

The nature of discovered anomalies in heat capacity is still unknown.

For the moment we have no additional information about the anomaly at 30 K. The $\lambda$-like anomaly at $\sim 60$ K might display some long range ordering in the substance. Its temperature is close to temperature $T_s$, where the total entropy of Cr(AA)$_3$ crystal has the maximal temperature derivative. The collective long range ordering in solids is often having been detected at that temperature $T_s$, where the derivative of the total entropy in temperature is maximal (see, for example, superconducting effect in HTSC or the ordering of another nature in Refs. [12]–[15]).

The magnetic susceptibility data show that the anomalies in the heat capacity do not result from any magnetic phase transitions. Then, one can suppose the anomaly to result from the change in the structure of the crystal or of the molecule. But in Raman spectra no significant change indicative of structural transformation in the crystal (of phase transition) was observed. That’s why the crystal is’nt thought to be arranged as a whole. In this case one may expect a rearrangement or an ordering of the loosely bound atoms or separate structural fragments: molecules Cr(AA)$_3$, ligands $C_5H_7O_2$ or groups $CH$ and $CH_3$.

The analysis of the internal vibrations of the molecule in Raman spectra has shown no change in structure of molecule with temperature. The absence of magnetic anomalies testifies that the symmetry of ion Cr$^{3+}$ crystal surrounding does not change substantially within the temperature range under investigation. This means that the change in geometry of molecule is hardly probable in the vicinity of chromium ion. One should rather
expect some change connected with the dynamics of the methyl groups.

The torsional vibrations of methyl groups were identified in Raman spectra of \textit{Al–} and \textit{Ga–} \(\beta\)-diketonates \cite{10}. They were detected below \(77\, K\) in the frequency region \(100 - 140 \, \text{cm}^{-1}\). One may suppose that just as in Ref. \cite{16} the new band \(109 \, \text{cm}^{-1}\) appeared in Raman spectra of \(\text{Cr(AA)}_3\) below \(60 \, K\) (Fig.5) results from the scattering on the torsional vibrations of the methyl groups. Only these vibrations can show an observed temperature behavior of the line intensity in Raman spectra.

According to Bose–Einstein distribution the function \(\phi(z)\) entering in the general expression for the heat capacity and characterizing the statistical weight of vibrational modes is

\[
\phi(z) = \frac{z^2 e^{-z}}{(1 + e^{-z})^2}, \quad z = \frac{\hbar \omega}{kT}.
\]

The maximal change of statistical weight of vibrational mode \(\hbar \omega\) occurs at the temperature \(T = \frac{\hbar \omega}{3k}\). Then the maximal change of the statistical weight of the torsion vibrations \(109 \, \text{cm}^{-1}\) (\(\sim 157\, K\)) falls at \(\sim 52\, K\). It is interesting to note that this value is close to the temperature of the anomaly in heat capacity (\(\sim 60 \, K\)).

This \(\lambda\)-like anomaly (Fig.1) might display some long range ordering all over the crystal below \(\sim 60 \, K\). The torsional vibrations of the methyl groups observed in Raman spectra at low temperatures arise at the same temperature \(\sim 60 \, K\). The assumed long range ordering might be attributed just to the dynamics of the methyl groups.

Within the temperature range \(110 - 240 \, K\) the diffuse anomaly in heat capacity takes place. Within the same temperature range (120–210 K) the smooth change in the sample color has been detected. When temperature decreases from \(300 \, K\) to \(78 \, K\) the ESR spectra exhibit the broadening of lines without any change of their energetic position (Fig.3). Such a broadening might be explained by the appearance of additional indirect anisotropic interaction which results from the decrease of the mobility of separate fragments of \(\text{Cr(AA)}_3\) molecule with temperature. This broadening is observed within

Figure 5: \textit{Raman spectra of \text{Cr(AA)}_3.}
change in the sample color take place. The magnetic susceptibility shows the weak deviation of experimental points from the Curie–Weiss low within the same temperature range 140 – 190 K.

One can suppose that ions Cr$^{3+}$ responsible for the paramagnetic behavior of Cr(AA)$_3$ crystals might be slightly affected by the change of some fragments of Cr(AA)$_3$ molecule with temperature. The change of energetic state of these fragments might result in the small perturbation of the crystal field. The last results in redistribution of electron density, shift of the transmission spectra and change in color of crystals when temperature varies from liquid nitrogen to room one.

4 Conclusion

In the present study some effects have been discovered in the low temperature properties of chromium tris–acetylacetonate Cr(AA)$_3$, which have not been observed before: the effect of thermochromism and three anomalies in heat capacity.

Anomalies in heat capacity generally display some transformations in a substance.

There are no considerations as regards the anomaly at 30 K.

As for the 60 K–anomaly, the assumption has been put forward that it might display some long range ordering taken place in the CH$_3$– subsystem at this temperature. The rise of torsional vibrations of CH$_3$– methyl groups at the same temperature was the basis for this assumption.

Besides, it was detected that the wide diffuse anomaly in the temperature range 110 – 240 K was accompanied with some features in ESR– and transmission spectra, with weak deviation of the magnetic susceptibility from the Curie–Weiss low, and change in color of the sample in the same temperature range. All these features were assumed to be attributed to a change with temperature of some fragments of the Cr(AA)$_3$ molecule which are still to be recognized.

To verify our tentative insight into the nature of discovered effects the complex investigation of β–diketonates of other transition metals with different ligands should be carried out.

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