Low-Temperature Thermochromism of Chromium *tris*-Acetylacetonate and the Anomaly of Specific Heat within the Range 30−210 K

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Abstract

Two anomalies with the maxima at 30 and 60 K are discovered in low-temperature specific heat of chromium *tris*-acetylacetonate $Cr(AA)_3$, as well as a diffuse anomaly within the range 110−220 K. Besides, a reversible change of colour of $Cr(AA)_3$ crystals during their cooling till liquid nitrogen temperature is discovered (thermochromism). It is stated that the reversible thermochromism is observed for the major part of β-diketonates of transition metals. In order to reveal the nature of this phenomenon, we measured static magnetic susceptibility within the range 2−300 K, recorded ESR spectra at Cr^{3+} ion and absorption spectra in visible region. The analysis of the data obtained allows us to assume that orientation ordering of CH_3 groups occurs in the crystals of β-diketonates of transition metals when temperature is decreased.

INTRODUCTION

Chromium *tris*-acetylacetonate $Cr(C_5H_7O_2)_3$, or $Cr(AA)_3$, belongs to the class of β-diketonate complexes of transition metals that crystallize in the lattice of molecular type. Metal β-diketonates $Me(AA)_3$ are widely used as catalysts, to separate metals, to deposit metal and oxide coatings. The range of their applications is getting broader permanently which stimulates their further investigation. The complexes $Me(AA)_3$ have been thoroughly studied in the aspects of thermodynamics [1−3] and crystal chemistry [4]. Recently they have become the subject of theoretical investigations [5, 6]. We discovered the effects that were not observed before in metal β-diketonates. In the present paper we describe two effects: 1) anomalies in low-temperature specific heat; 2) reversible change in the colour of crystals when cooled till liquid nitrogen temperature (thermochromism).

EXPERIMENTAL

The sample of $Cr(AA)_3$ was synthesized according to the known techniques starting from $CrCl_3 \cdot 10 H_2O$ and the ligand (HAA) neutralized by NaOH. The synthesis was conducted in aqueous alcohol medium. The resulting compound, purified by vacuum sublimation, is crystal powder with the linear mean crystallite size of 0.3−0.5 mm. The colour of $Cr(AA)_3$ at room temperature is violet. The compound was characterized by means of chemical analysis, IR spectroscopy, derivatography and X-ray diffraction patterns.

We measured the specific heat of $Cr(AA)_3$ by adiabatic method at 107 points of the temperature range 5−320 K using calorimetric set-up which was characterized in [7, 8]. Several anomalies were detected in specific heat. They include an anomaly with a clearly exhibited maximum at 60 K, a broad anomaly within the range 110−220 K and a small peak at 30 K (Fig. 1). Anomalous component of specific heat $\delta C(T)$ at the maximum accounts for 1, 3.2 and 0.33 % of regular specific heat, respectively. The contributions into entropy ΔS that are connected with anomalies are, J/(mol·K): 0.07 (30 K), 1.20 ± 0.05 (60 K), 1.5 ± 0.25 (a broad anomaly). The anomalous component $\delta C(T)$ was obtained

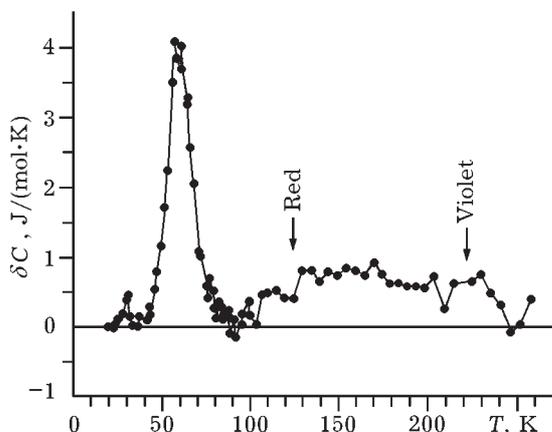Fig. 1. Anomalous component of specific heat $\delta C(T)$ of $Cr(AA)_3$.

by subtracting the regular specific heat from experimental one. Regular specific heat was determined using the technique de- scribed in [9, 10].

In order to reveal the nature of the discovered anomalies, we measured static magnetic susceptibility, ESR spectra from Cr^{3+} ion, absorption spectra in the visible region, and followed the changes in colour of $Cr(AA)_3$ crystals while temperature was changed from 78 to 300 K.

Static magnetic susceptibility of $Cr(AA)_3$ within the temperature range 2−300 K was measured with a SQUID magnetometer MPMS-5s of the Quantum Design Co. (Fig. 2). Effective magnetic moment at 300 K was 3.83 Bohr's magne-
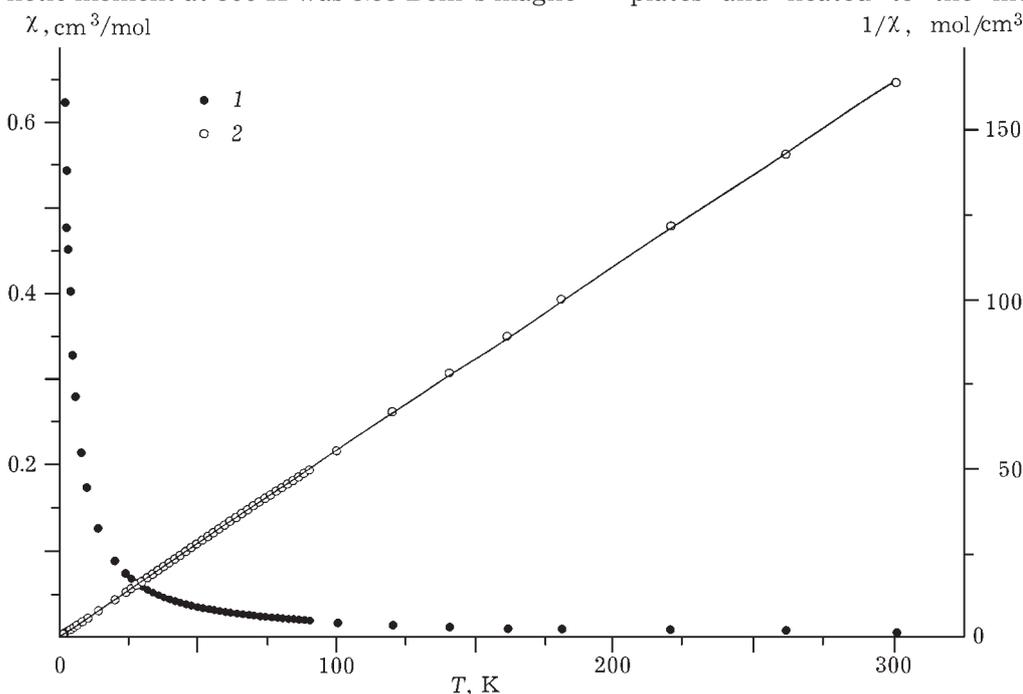
tons. Experimental points within the temperature range investigated are well fitted by the Curie − Weiss law. No noticeable magnetic anomalies are observed.

ESR spectra from Cr^{3+} ion in $Cr(AA)_3$ single crystal were recorded with E-109 spectrometer of Varian Co. at the frequency of 9.5 GHz within the temperature range 78−300 K. The main orbital state for the octahedral surrounding of the Cr^{3+} ion in $Cr(AA)_3$ crystal is singlet; g-factors for the $3d^3$ configuration of Cr^{3+} ion are close to the value $g = 2$ [11]. The observed large anisotropy of ESR spectra of Cr^{3+} ion in $Cr(AA)_3$ single crystals is conditioned by large shifts of the spectrum due to large second-order corrections for the description of hyperfine splittings for the case of initial splittings comparable with the Zeeman interaction. The decrease of temperature from 300 to 78 K leads to the broadening of lines without changing their positions (Fig. 3). For some lines, such a broadening leads to their complete disappearance.

Absorption spectra of $Cr(AA)_3$ within the frequency range 11 000−30 000 cm^{-1} were recorded at room temperature and at liquid nitrogen temperature with a two-ray spectrophotometer Specord UV-200. The sample was prepared from powder placed between two quartz plates and heated to the melting point of
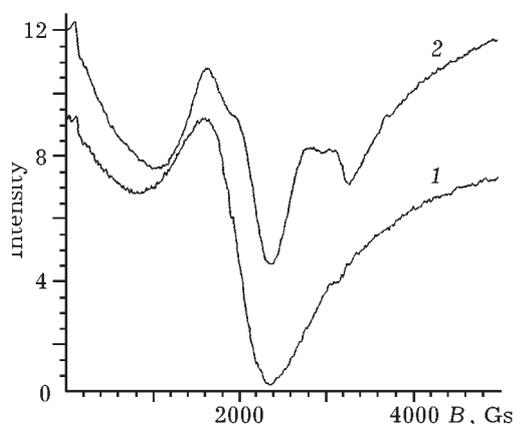

Fig. 2. Magnetic susceptibility χ (*1*) and inverse susceptibility $1/\chi$ (*2*) as functions of temperature for $Cr(AA)_3$. $\chi = 1.831/(T + 0.56)$.

Fig. 3. ESR spectra from Cr^{3+} ion at different temperatures, K: 78 (*1*) and 300 (*2*).

$Cr(AA)_3$ (T_{melt} = 489 K). A continuous layer ~ 0.01 mm thick was formed during cooling. The spectra are shown in Fig. 4. Comparison shows that the maximum of absorption band (18 100 cm^{-1}) is shifted by 600 cm^{-1} to higher frequencies when temperature is changed from room to liquid nitrogen. This shift exceeds the expected one connected with thermal expansion of the lattice.

The sample is dark-violet at room temperature. When immersed into liquid nitrogen, it becomes red (thermochromism). This change of colour is reversible. A special experiment was made to observe the change of colour with changing temperature. The sample fixed on a copper substrate was immersed in the bath with liquid nitrogen. The temperature of the substrate and the sample could be increased slowly from 78 to 300 K. Temperature was measured with a thermocouple (copper-constantan). The colour of the sample (red) did not change noticeably when temperature was increased from 78 to 120 K. T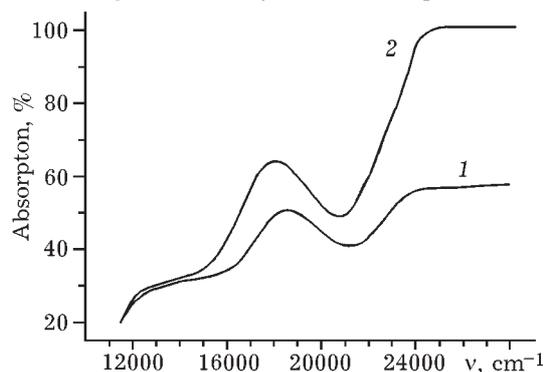he colour is observed to change smoothly when temperature increases from 120 to 210 K. At 210 K, the sample gets dark-violet. Its colour does not change any more during further increase of temperature.

An additional experiment showed that the reversible thermochromism is observed for the majority of β-diketonates of transition metals when cooling them with liquid nitrogen. We tested 36 complexes. The major part of complexes gets lighter with decreasing temperature. The sharpest changes of colour are observed for the compounds of cobalt (III), copper (II) and chromium (III): $Co(AA)_3$ which is dark-green at room temperature gets dark-violet when put into liquid nitrogen. Copper (II) acetylacetonatehexafluoracetylacetonate $Cu(AA)_3(HFA)$ which is green at room temperature becomes blue in liquid nitrogen. The change of colour for $Cr(AA)_3$ was described above.

RESULTS AND DISCUSSION

Anomalies in specific heat usually depict some transformations in the substance. The nature of anomalies discovered by us is unknown yet. The data on magnetic susceptibility allow us to state that the anomalies discovered in specific heat are not connected with any magnetic phase transitions. One can assume that the anomalies are due to the changes in the structure of crystal or molecule. The necessary condition for structural changes to be possible in solid at low temperatures is the presence of atoms or structural fragments of the lattice weakly bonded to each other. There are such fragments in the $Cr(AA)_3$ crystal. They include: $Cr(C_5H_7O_2)_3$ molecule, $C_5H_7O_2$ ligands, as well as CH and CH_3 groups (Fig. 5). Since heat and entropy effects observed in specific heat are small, the expected changes can be connected with rearrangement or disordering of separate structural fragments but not the whole crystal.

The absence of magnetic anomalies points to the fact that the symmetry of crystal surroundings of Cr^{3+} does not undergo any substantial changes within the temperature range under investigation. Because of this, the change of molecule geometry directly in the vicinity of chromium ion seems improbable. In the present case one could better expect changes connected with the dynamics of methyl groups. Torsion
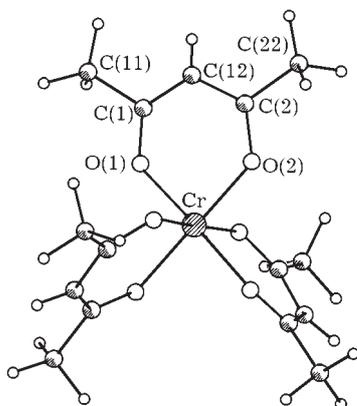

Fig. 4. Absorption spectra of a thin layer of $Cr(AA)_3$ in the visible region at temperatures of 78 (*1*) and 300 K (*2*).

Fig. 5. The structure of $Cr(C_5H_7O_2)_3$ molecule.

vibrations of methyl groups of some β–diketonates were identified in [12] by means of Raman spectroscopy. These vibrations are localized in the frequency region of $100-140$ cm^{-1} depending on the kind of metal and ligand. According to the features of Bose distribution, the function $\varphi(z)$ included in the overall equation for specific heat which characterizes the possibility of thermal excitation of the vibration modes in crystal can be written as $\varphi(z) = (z/2)^2/Sh^2(z/2)$, where $z = \hbar\omega/(kT)$. It follows from this equation that a maximum change of the probability of thermal excitation of vibration modes with the energy $\hbar\omega$ occurs at $T = \hbar\omega/(3k)$. Since the frequencies of methyl group torsion vibrations are ~120 cm^{-1} (~180 K), a sharp decrease in the probability of their thermal excitation occurs at 60 K. As a result, a collective orientation ordering of methyl groups over the whole crystal can take place under the action of some weak interactions. This ordering will be exhibited in specific heat as a phase transition at 60 K.

The collective ordering with the formation of long-range order in solids at low temperatures is observed at a temperature T_s at which the total entropy of the crystal has a maximum derivative with respect to temperature (for example, superconductivity in HTSC (High Temperature Superconductor) or the ordering of another nature [13−16]). In the case under consideration, for $Cr(AA)_3$, T_s is practically equal to the temperature at which the anomaly is observed (60 K). This coincidence can be considered as an additional argument in favour of the assumption concerning the formation of long-range order in the $Cr(AA)_3$ crystal under investigation.

The decrease in temperature from 300 to 78 K causes broadening of lines in ESR spectra without any changes in their position with respect to energy (see Fig. 3). One of the possible explanations of this broadening of ESR lines in this case can be connected with the appearance in additional channels of indirect anisotropic interaction which is realized due to the decrease in the mobility of separate fragments of $Cr(AA)_3$ molecule while temperature is decreased. It is observed in quite the same temperature range as a diffuse anomaly in specific heat $(110-220$ K).

A smooth change in the sample colour is also observed in the same temperature range $(120-210$ K). If we consider the plot of magnetic susceptibility attentively (see Fig. 2) we can see that there is a slight deviation of experimental points from the Curie − Weiss law within the range $140-190$ K. This means that the Cr^{3+} ion which is responsible for the paramagnetic behaviour of $Cr(AA)_3$ crystals feels a slight influence of the changes that occur with methyl groups when temperature is changed within this range. It is possible that the change in the energy state of methyl groups causes perturbation of the inner crystal field and leads to small deformation of the molecule structure (for example, to the deformation of the chelate ring). This leads to the redistribution of electron density, shift of absorption spectrum and change in the colour of crystals when temperature is varied within the range $78-300$ K.

The hypothesis should be subjected to verifying and further investigation, as well as the nature of a small anomaly at 30 K.

CONCLUSIONS

In the present work we discovered the effects that were not observed for chromium *tris*-acetylacetonate $Cr(AA)_3$ before, thermochromism and the anomalies in specific heat. Besides, the accompanying features of ESR spectra and absorption spectra at low temperatures are discovered. The hypothesis is put forward concerning the connection between the discovered effects and thermal excitation of vibration degrees of freedom of methyl groups and the possibility of their orientation ordering at temperatures below 60 K.

For further investigation of the nature of these effects, it is assumed to conduct a complex study of the properties of β-diketonates of other transition metals with different ligands.

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