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Abstract

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APPEARANCE OF FINE STRUCTURE IN THE E.P.R. SPECTRUM OF CHROMIUM OXIDE DOPED WITH Li^+ IONS

(Presented by Academician A. A. Balandin, 13 V 1964)

In work (1) it was found that, in the reaction of various potassium compounds with CrO_3 at high temperatures, the products formed give a very complex e.p.r. spectrum. It was assumed that such a spectrum is due to the fine structure of the Cr^{3+} ion; however, the question remained unclear as to why the fine structure is preserved in a matrix of Cr_2O_3.

To clarify this question, and also the possibility of obtaining such spectra for products of the interaction of CrO_3 with salts of other monovalent ions, in the present work we investigated the products of the reaction of CrO_3 with $LiNO_3$.

Table 1

$H_{res} KCr(SO_4)_2 \cdot 12H_2O \delta =$ 0.130 $cm^{-1} g = 1.99$	$H_{res} Cr_2O_3{-}Li_2O$
$H \perp$ (111)20002860339037704800	$\leftarrow\perp$ 20902710$\leftarrow - \perp -$3340
$H \perp$ (110)252027403300357038704100	3470

The reaction was carried out in the solid phase in air at a rate of temperature rise of ~ 7 deg/min, and the mixture was held for 1 hour at 800°. Some samples were obtained under the same conditions, but in a hydrogen atmosphere. The concentration of Li_2O in the final mixture was 0.01; 0.1; 0.5; 1.0; 3.0; 5.0; 10.0; 15.0 wt. %. The e.p.r. spectra were recorded on an RE-1301 apparatus with $\nu = 9326$ MHz at $t = 20,\ 150,\ -196°$. The magnetic susceptibility was measured by the Faraday method in the interval $H = 1500$–4500 oersted and $t = 20$–$160°$. The electrical conductivity of some samples was studied at direct current in vacuum of 10^{-5} mm Hg and in the interval $t = 20$–$300°$.

Figure 1 shows the e.p.r. spectra of samples containing 0.1–15 wt. % Li_2O. All the e.p.r. spectra (except the spectrum of the sample with 15 wt. % Li_2O) have an appearance clearly reminiscent of the fine structure (f.s.) of the Cr^{3+} ion in chromium-potassium alum. Indeed, from the data given below (Table

1) it is seen that the maxima of the absorption lines observed by us coincide with the maxima calculated for $KCr(SO_4)_2 \cdot 12H_2O$. Consequently, the complex character of the e.p.r. spectrum of Cr_2O_3 samples doped with Li_2O is indeed associated with the fine structure of the Cr^{3+} ion. In this connection it is necessary to answer two questions: first, in which sites of the crystal lattice are the Cr^{3+} ions located that give rise to the f.s. of the e.p.r. spectrum, and what role is played by the Li^+ ions; second, why the f.s. is observed in a magnetically concentrated system, in which exchange and dipole-dipole interactions are strong.

In chromium-potassium alum the Cr^{3+} ions are in the cubic crystal field of an octahedron of H_2O molecules. The presence of an axial component leads to splitting of the levels in zero field and to the appearance of f.s. Consequently, in Cr_2O_3—Li_2O samples part of the Cr^{3+} ions must be located in fields of the same symmetry. This is easily realized in the given system, since it is well known (3) that the interaction of lithium salts with Cr_2O_3 at high temperatures leads to the formation of the $LiCrO_2$ structure. Of the samples studied, the sample with 15 wt. % Li_2O corresponds exactly to such a compound. The arrangement of Cr^{3+} and Li^+ ions in such a structure is shown in Fig. 2, *a**, from which it is seen that the Cr^{3+} ions and the Li^+ ions occupy oc-

* The figure shows one half ($c/2$) of the hexagonal unit cell of $LiCrO_2$.

Table 2

Dependence of the physical properties of the specimens on the content of Li_2O

	Concentration of Li_2O, wt.%							
	0	0.01	0.1	1.0	3.0	5.0	10.0	15.0
$\chi^* \cdot 10^6$	25.7	25.6	48.2	72.1	89.2	87.5	51.0	26.0
$\lg \rho_{5150^\circ C}$	12.5	–	–	–	6	–	–	–
E_σ, eV	1.40	–	–	–	0.33	–	–	–
Color	Light green	Light green	Green	Dark green	Black	Black	Dark green	Green

* The value of χ is given for $H = 3500$ oersted; specimens with 0.1-10% Li_2O are ferromagnetic.

tetrahedral voids. However, this unit cell is much more complex than the cell of chromium-potassium alum (Fig. 2, c), and the Cr^{3+} ions in it cannot give an e.p.r. spectrum similar to the spectrum of alum.

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

The conditions under which the investigated specimens were obtained apparently led to part of the Li^+ ions being used not for the formation of $LiCrO_2$ compounds, but entering the interstices of the Cr_2O_3 lattice, causing strong oxygen absorption by the specimens. The formation of a large amount of nonstoichiometric oxygen led to a sharp increase in magnetic susceptibility and electrical conductivity, as is seen from the data of Table 2; the largest amount of nonstoichiometric oxygen is present in specimens with a content of 3 and 5 wt.% Li_2O.

Under these conditions, apparently, a structure is readily formed with an excess of oxygen ions and with an arrangement of Cr^{3+} ions analogous to their arrangement in alums (Fig. 2, b), while the remaining Cr^{3+} ions (Fig. 2, a) are oxidized to Cr^{6+} ions, indicated in Fig. 2, b by dots.

Fig. 1. E.p.r. spectra of Cr_2O_3 specimens containing additions of Li_2O: 1 –0.1%; 2 –1%; 3 –3%; 4 –5%; 5–10%; 6 –15% Li_2O

Fig. 2. Structure of the unit cell of $LiCrO_2$ and $KCr(SO_4)_2 \cdot 12H_2O$. a –unit cell of $LiCrO_2$ (half); b –possible arrangement of the ions in the "defective" $LiCrO_2$ structure; c –unit cell of $KCr(SO_4)_2 \cdot 12H_2O$

Consideration of Fig. 3 shows that the f.s. of the e.p.r. spectra is indeed associated with nonstoichiometric oxygen. Specimens with a content of 3 and 5 wt.% Li_2O, prepared in an H_2 atmosphere, give only a narrow e.p.r. line without f.s. (Fig. 3, 1 and 4). Heating the obtained specimens in an air stream leads to the appearance of f.s. A decrease in the amount of nonstoichiometric oxygen and, correspondingly, a decrease in f.s. also occurs upon introducing increasing amounts of Al^{3+} ions into the specimens (Fig. 4), which hinder the penetration of Li^+ ions into the interstices of the Cr_2O_3 lattice.

The introduction of Li^+ ions into the Cr_2O_3 lattice leads not only to the appearance of nonstoichiometric oxygen, but also substantially affects the indirect ex –

exchange interaction in Cr_2O_3 and the formation of an antiferromagnetic structure. The presence of Li^+ ions in the Cr_2O_3 structure leads to the disappearance of long-range antiferromagnetic order and to a strong shift of the transition point toward low temperatures. Such a weakening of the exchange interaction makes it possible to observe h.f.s. in the EPR spectra. The antiferromagnetic interaction appears at low temperatures, and this leads to a smearing of the h.f.s. in the EPR spectra.

The Li^+ ions prevent the formation of long-range antiferromagnetic order, but the indirect exchange interaction in the chain Cr^{3+}—O^{2-}—Cr^{3+} remains to some extent. The presence of such exchange is confirmed by the small line width (130 oersted) of the sample with 15 wt.% Li_2O (Fig. 1), which in the case of dipole-dipole interaction should have been about 1200 oersted.

Fig. 3. EPR spectra of Cr_2O_3—Li_2O samples obtained in H_2 and treated with air.
1 –3% Li_2O in an H_2 atmosphere at 800°C; 2 –the same, heated at 800° for 1 hour in air; 3 –the same at 900° for 2 hours in air; 4 –5% Li_2O in an H_2 atmosphere; 5 –the same, heated at 800° for 2 hours in air.

Fig. 4. Influence of additions of Al^{3+} ions on the form of the EPR spectra of a Cr_2O_3 sample containing 3 wt.% Li_2O.
1 –3%; 2 –6%; 3 –12% Al_2O_3.

The detailed mechanism of the influence of Li^+ ions on the exchange interaction in Cr_2O_3 is still not clear; however, it may be assumed that the interaction of Li^+ ions with oxygen ions to some extent prevents the participation of the oxygen *p*-electrons in the indirect exchange interaction.

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