ELECTRON PARAMAGNETIC RESONANCE OF Cr^{+3} ION IN $LiCrO_2$

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The electron spin resonance measurements were performed in order to investigate the electronic g factor and the effective magnetic moment μ_{eff} of a $LiCrO_2$ polycrystal and to determine the EPR line shape. From the resonance field obtained by the present experiment, the electronic g factor and the effective magnetic moment μ_{eff} for this compound were calculated to be 1.975 ± 0.035 and 3.8258 μ_B, respectively. The Lorentzian shape of the EPR line was determined by the least squares method.

1. Introduction

$LiCrO_2$ is an antiferromagnet ($T_N = 200$ K, $\theta = -550$ K), which belongs to a hexagonal space group, $R\bar{3}m$ [1] with the Cr^{+3} ions on sites of D_{3d} symmetry (Fig. 1). The ground state of the trivalent chromium ion in this symmetry corresponds to the orbital singlet $3d^3\,{}^4F_{3/2}$ ($S = 1, L = 3$). Fig. 2 shows the energy-level diagram for the d^3 configuration in the case of the distortion of the octahedron with axial symmetry along a trigonal axis [1].

Details of the $LiCrO_2$ single crystal absorption spectrum experiment are presented in paper [2]. This spectrum has been measured at 300, 80 and 15 K. The allowed spin transitions ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{ig}$ were observed at $\sim$17500 and 24000 cm^{-1}, respectively. The forbidden spin transitions ${}^4A_{2g} \rightarrow {}^2E_g$, ${}^4A_{2g} \rightarrow {}^2T_{1g}$ and ${}^4A_{2g} \rightarrow {}^2T_{2g}$ show an anomalous intensity vs. temperature dependence. The first-order trigonal field parameter was estimated to be $\sim$600 cm^{-1}. A trigonal field of this strength would split the ${}^2E$ level into a doublet separated by $\sim$25 cm^{-1}, ($\lambda = -4/3\,\zeta\,(E({}^2E)-E({}^2T_2))$ with $\zeta = 170$ cm^{-1}, $E({}^2E)$ and $E({}^2T_2)$ equal to 14250 and 19500 cm^{-1}, respectively. The value of the Racah parameter B was calculated to be 600 cm^{-1}, using the ${}^4T_1({}^4P, {}^4F)$ energy matrix and the value of 1750 cm^{-1} = 10 Dq. The nephelauxetic ratio $\beta = B/B_0$, with $B_0 = 918$ cm^{-1} is 0.660.

Paper [3] presents the magnetic ordering, magnetization, susceptibility and Mössbauer measurements for $LiCr_{1-x}Fe_xO_2$ system with $x = 0, 0.1, 0.2, \ldots 0.9, 1.0$. The

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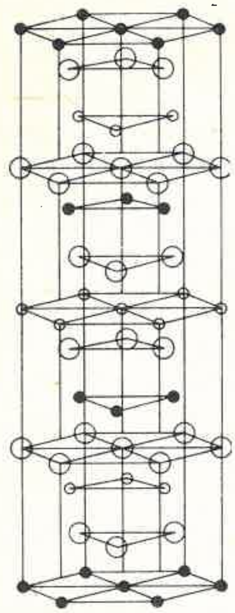

Fig. 1. The crystal structure of $LiCrO_2$. Large open circles are O, small open circles are Li, small filled circles, Cr

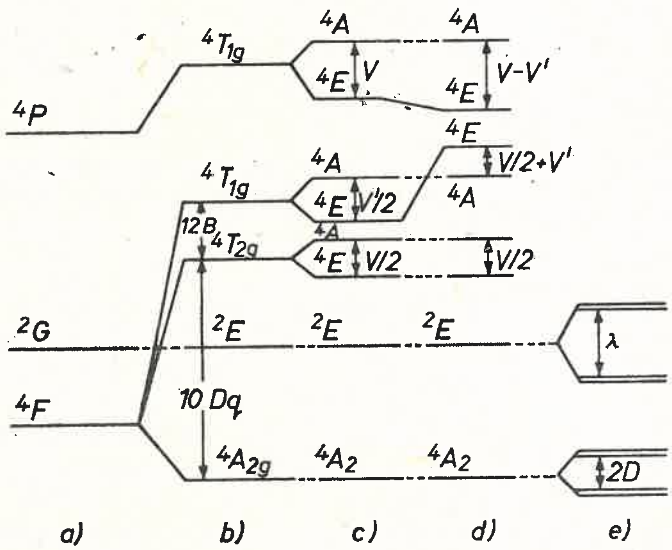

Fig. 2. Energy-level diagram for chromium (III) in octahedral and weak trigonal fields: a) — free ion, b) — octahedral field, c) — first order positive trigonal field, d) — second order trigonal field, V' — negative, e) — trigonal field and spin-orbit coupling

susceptibility of $LiCrO_2$ above 450 K obeys a Curie-Weiss law. A least-squares fit to the data gives a paramagnetic Curie-Weiss point, $\theta = -570$ K. The magnetic moment of $3.55 \pm 0.11\ \mu_B$ is in agreement with 3.71 μ_B obtained by Bongers [4]; his θ value, -577 K, differs by only 7 K. The negative Curie-Weiss temperature shows that the dominant magnetic interactions are antiferromagnetic in nature. Below 250 K the susceptibility curve changes slope and declines sharply until 12 K, below which the curve is almost flat down to 4.2 K. This temperature-independent behaviour suggests that the Cr spins are parallel to the $\hat{c}$ axis.

The details of EPR spectrum for the Cr^{+3} ion in the $LiCrO_2$ powder are presented in this paper.

2. *Experimental results and discussion*

The EPR spectrum of Cr^{+3} ion in the $LiCrO_2$ powder was measured at room temperature and at the frequency of 9.4738 GHz, a SEX/28 type microwave EPR spectrometer was equipped with 100 kHz field modulation. The spectrum was recorded in the first derivative absorption line (Fig. 3). As shown in that figure, the spectrum is very simple, since it is composed of one line only, described by the Hamiltonian $\mathscr{H} = g\beta\vec{H}\cdot\vec{S}$ ($S = 3/2$). The resonance field $\vec{H}$ was 3427.3707 Gs, from which the value of $g(^4A_2)$ was calculated to be 1.975 ± 0.035 by using the formula $g\mu_B\vec{H} = h\nu$ where g is the electronic factor, μ_B is the Bohr magneton, $\vec{H}$ is strength of the magnetic field, h is Planck's constant and ν is the microwave frequency of the spectrometer. This g value is close to 2 and so the origin

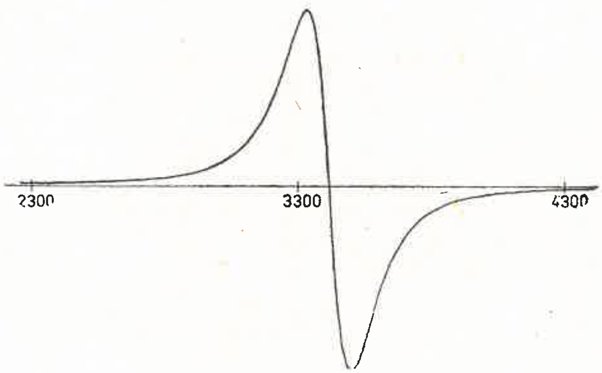

Fig. 3. The EPR spectrum of Cr^{+3} ion in the $LiCrO_2$ powder ($T = 300$ K)

of the magnetic moment of $LiCrO_2$ is considered to almost depend on the spin angular momentum of Cr ion.

The effective magnetic moment of the A state is determined by formula $\mu_{eff} = \mu_B g\sqrt{S(S+1)}$ ($S = 3/2$). Using the experimental g-value the effective magnetic moment for our case has been estimated as 3.8258 μ_B, while the pure-spin moment μ^0_{eff} equals 3.8788 μ_B. A small difference, $\mu_{eff}(\exp) - \mu^0_{eff} = -0.0529\ \mu_B$, is additional evidence for small spin-orbit coupling effect. Our μ_{eff} — value is in agreement with 3.71 μ_B obtained by Bongers [4].

The EPR line shape has been determined by the least-squares method [5] to be Lorentzian. Its width at half maximum intensity was estimated as ~ 300 Gs. This manifests the domination of the exchange interactions between the nearest electron spins over the spin--orbit coupling.

The experiments on the $LiCrO_2$ single crystal are expected to give more information on the subject.

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