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LETTER

Optical and magnetic properties of europium doped potassium rare earth double chromate $\text{KLa}(\text{CrO}_4)_2:\text{Eu}^{3+}$

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The double chromates of rare earth and alkaline cation have been synthesized for some years [1–3]. They crystallize into three different structural types [4–6]. Compounds with heavy rare earths (La–Eu) considered here, constitute the first isostructural series. The lanthanum–potassium compound crystallizes in the monoclinic system. The space group is $P2_1/c$. In that structure, the lanthanum atom is located in a $(\text{La}(\text{CrO}_4)_2)_n^-$ layer, perpendicular to the a crystallographic axis. Each layer is formed by double rows of two independent CrO_4^{2-} complex cations, linked to the rare earth by oxygen atoms. The lanthanum is ninefold coordinated. All atoms occupy the general 4e atomic position in the crystal lattice. The symmetry of the rare earth is C_1 .

Recently, some physico-chemical properties (IR and Raman spectra, magnetic properties) have been reported [7, 8]. This work is the first of a series studying the optical properties and simulating the energy levels scheme of Eu^{3+} embedded in rare earth–potassium double chromates within the crystal field theory frame. The paramagnetic susceptibility (and its variation versus temperature) is also calculated using the derived wavefunctions.

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Experimental

Polycrystalline powder samples were obtained according to the previously described method [4], by a hydrothermal synthesis at 150 °C in sealed glass tubes during one month, from a finely ground mixture of $\text{K}_2\text{Cr}_2\text{O}_7/\text{Ln}_2\text{O}_3$ in appropriated ratios. Different samples of $\text{KLa}(\text{CrO}_4)_2$ activated by 0.01 and 0.05 mol% of Eu^{3+} for optical measurements and pure $\text{KLa}(\text{CrO}_4)_2$ for optical as well as magnetic measurements were synthesized and checked by X-rays. At that point, it is interesting to underline that sometimes X-rays diffraction is not a powerful enough method for testing the degree of crystallinity. That is the case of the double chromates where the X-ray diffraction pattern is correct for the samples, but optical measurements give large fluorescence lines. Thus, the synthesis conditions have to be modified (refiring and regrinding), in order to get the fluorescence lines as narrow as possible.

The fluorescence emission of Eu^{3+} is obtained from excitation by the blue line of a CW-argon laser and/or from a continuous dye laser (Rhodamin-6G), accorded on the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition. It is measured on pure and doped compounds at room and liquid nitrogen temperatures.

The paramagnetic susceptibility (χ) measurements are performed between liquid helium and room temperature using a DSM-5 pendule magnetometer. The maximum magnetic field is 14 kG. The apparatus was calibrated with $\text{Hg}[\text{Co}(\text{SCN})_4]$. χ is found to be magnetic field independent. The diamagnetic correction is taken from measurements on $\text{KLa}(\text{CrO}_4)_2$.

Optical results

Analysis of the fluorescence spectrum

The fluorescence spectrum of $\text{KLa}(\text{CrO}_4)_2$ is due to emission from the $^5\text{D}_0$ resonance level. No line from upper levels ($^5\text{D}_1$ and $^5\text{D}_2$) is recorded. The fluorescence is not very intense, even for $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (Fig. 1). Lines are not narrow, indicating that a good crystallinity of the powder is not obtained (see before). $^5\text{D}_0 \rightarrow ^7\text{F}_3$ is difficult to record. A very low intensity of that transition has been recently reported and is related to a small J -mixing effect, itself a consequence of relatively small values of second and fourth order crystal field parameters [9]. The same feature occurs here. Many lines are accompanied by vibronic transitions whose frequencies have been previously recorded by the Raman technique [8].

Simulation of the energy level scheme

From the fluorescence measurements, we derive an energy level scheme of 24 $^7\text{F}_J$ Stark components

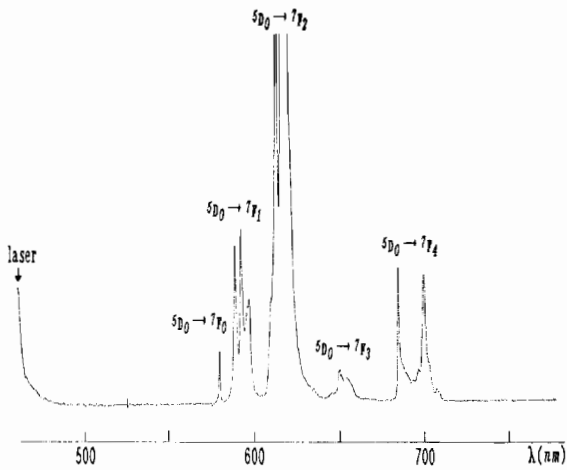


Fig. 1. Part of the emission spectrum of $\text{KLa}(\text{CrO}_4)_2:\text{Eu}^{3+}$ under excitation of the CW-argon laser blue line (77 K).

of the $4f^6$ configuration of Eu^{3+} , on which the crystal field simulation can be attempted. The simulation is performed considering C_{2v} as approximated symmetry. Not only the coordination polyhedron shows that it is a good approximation of the real symmetry C_1 , but it is also convenient, involving nine real crystal field parameters instead of 27 real and imaginary ones. The C_{2v} potential is written as

$$V_{C_{2v}} = B_0^2 C_0^2 + B_2^2 (C_{-2}^2 + C_2^2) + B_0^4 C_0^4 + B_2^4 (C_{-2}^4 + C_2^4) \\ + B_4^4 (C_{-4}^4 + C_4^4) + B_0^6 C_0^6 + B_2^6 (C_{-2}^6 + C_2^6) \\ + B_4^6 (C_{-4}^6 + C_4^6) + B_6^6 (C_{-6}^6 + C_6^6)$$

Eu^{3+} ion is very convenient for crystal field calculations. This is due to the fact that the ground state of the $4f^6$ configuration, 7F_1 is alone of multiplicity seven. This multiplet is well separated from the rest of the configuration (the energy difference ${}^7F_1 \leftrightarrow {}^5D_1$ is about $12\,000\text{ cm}^{-1}$). Thus, the mixing of the free ion states is small. It is not necessary to diagonalize the secular determinant of the full configuration, because the crystal field effect is well reproduced by a spin operator formalism. We consider a strongly reduced basis, involving only the 7F term, i.e. a 49×49 matrix for a low symmetry [10]. In that case, we only need to include 'buffer' parameters, one per J value and diagonal in M , whose purpose is to maintain the 7F_J calculated barycenter equal to its experimental value.

The refinement of the simulation is performed by the FORTRAN routine 'REEL' [11], adapted to that case, which runs easily on an AT-type PC. The final set of crystal field parameters is given in Table 1 and the list of experimental and calculated levels in Table 2. Due to the small number of fitted levels, the r.m.s. standard deviation is not very significant. However, a good value of the residue shows that

TABLE 1. Experimental crystal field parameters (units in cm^{-1})

$B_0^2 = -655.0 \pm 29$
$B_2^2 = 245.6 \pm 16$
$B_0^4 = -480.0 \pm 44$
$B_2^4 = -240.7 \pm 28$
$B_4^4 = -151.9 \pm 26$
$B_0^6 = -337.5 \pm 74$
$B_2^6 = 1225.1 \pm 31$
$B_4^6 = -660.9 \pm 28$
$B_6^6 = 450.1 \pm 29$
Residue = 996
$\sigma = 8.4$

TABLE 2. Experimental and calculated energy levels of $\text{KLa}(\text{CrO}_4)_2:\text{Eu}^{3+}$ (units in cm^{-1})

	Exp.	Calc.	Exp. - Calc.
7F_0	0	0	0
	261	257	4
7F_1	366	364	2
	503	507	-4
	922	928	-6
	1022	1018	4
7F_2	1061	1062	-1
	1091	1092	-1
	1148	1140	8
		1797	
		1816	
	1855	1861	-5
7F_3	1868	1873	-5
	1888	1885	3
	1955	1957	-2
	2019	2002	17
	2635	2632	3
	2693	2684	9
	2754	2752	2
	2822	2835	-13
7F_4	2885	2884	1
	2949	2937	12
	2966	2975	-9
	3010	3009	1
	3144	3144	0
5D_0	17260	-	

the simulation is satisfying. The relatively small values of second and fourth rank crystal field parameters induce a small J -mixing effect, and explain the difficulty in recording the ${}^5D_0 \rightarrow {}^7F_3$ transition.

Paramagnetic susceptibility calculation

The paramagnetic susceptibility is calculated by the Van Vleck formula, derived from the perturbation theory [10].

TABLE 3. Experimental and calculated paramagnetic susceptibility versus temperature (in 10^3 emu mol $^{-1}$ units)

Temperature (K)	χ_{exp}	χ_{calc}
4.2	6.17	6.24
13	6.17	6.24
19	6.17	6.24
31	6.17	6.24
36	6.17	6.24
41	6.17	6.24
51	6.17	6.24
61	6.17	6.24
71	6.19	6.24
81	6.15	6.22
91	6.17	6.19
101	6.17	6.16
121	6.08	6.06
141	5.98	5.92
161	5.87	5.75
180	5.69	5.57
200	5.51	5.38
220	5.36	5.19
240	5.18	5.01
260	5.09	4.83

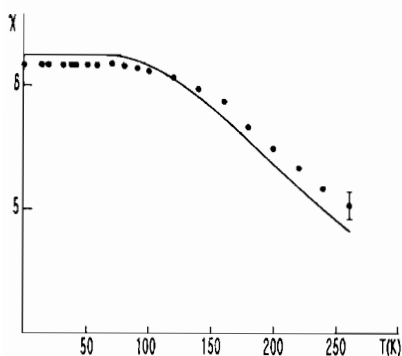


Fig. 2. Calculated and experimental paramagnetic susceptibility vs. temperature (χ in 10^3 emu mol $^{-1}$ units).

$$\chi = N\beta^2 \sum_i \frac{[E_i^{(1)}]^2 / kT - 2E_i^{(2)}}{E_i - E_j} B_i$$

$$E_i^{(1)} = \langle \phi_i | L + g_e S | \phi_i \rangle$$

$$E_i^{(2)} = \sum_{i \neq j} \frac{\langle \phi_i | L + g_e S | \phi_j \rangle \langle \phi_j | L + g_e S | \phi_i \rangle}{E_i - E_j}$$

In that expression N is the Avogadro number, β the Bohr magneton and B_i the thermal population of the i th energy level. $E^{(1)}$ and $E^{(2)}$ are the first order and second order perturbation terms, respectively, of the magnetic dipolar operator $L + g_e S$ applied on the non-perturbed wavefunctions ϕ .

The paramagnetic susceptibility of the $4f^6$ configuration of Eu^{3+} constitutes a very peculiar example of the Van Vleck paramagnetism. At low temperature, only the ground level, 7F_0 , is thermally populated. This level being non-magnetic, the value of the paramagnetic susceptibility is given by the second order term $E^{(2)}$. This term, temperature independent, creates a paramagnetic plateau whose position strongly depends on the wavefunction composition and on the energy difference between 7F_0 and other 7F_j crystal field levels, essentially those of 7F_1 .

For a calculation as realistic as possible, the wavefunctions are described on a more extended basis than the $|{}^7F_j\rangle$ basis used for the crystal field calculation. We consider a $4f^6$ secular determinant truncated at 671 $|\alpha SLJM\rangle$ states, far from the configuration degeneracy (3003), but large enough for that purpose [13]. The calculation is performed by the routine REEL. The crystal field parameters are those deduced from the optical data. The free ion parameter values are set to standard values [14], i.e. $E_0 = 2903$, $E_1 = 5444$, $E_2 = 24.83$, $E_3 = 585$, $\alpha = 20$, $\beta = -640$, $\gamma = 1750$ and $\zeta = 1285$ (cm^{-1} units). Table 3 gives the calculated and experimental values of χ .

The position of the plateau is very well reproduced (Fig. 2). At higher temperatures, there is a small discrepancy, always within the experimental error. This fact is common for most paramagnetic susceptibility simulations. It has to be connected with a smooth variation of the crystal field parameters with temperature (the c.f.p. set is calculated from the data recorded at 77 K).

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