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A direct calculation method for spectral parameters of the transition between 4T_2 and 4A_2 in chromium-doped crystals

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Abstract. A method for directly calculating the Huang–Rhys S -factors and the effective phonon energy $\hbar\omega$ as well as the linewidths of 4T_2 emission in chromium-doped oxides and fluorides is introduced. By use of this method, the experimental data required are only the wavelengths of the absorption and the emission peaks of the transitions between 4T_2 and 4A_2 . The calculated values agreed very well with the experimental data published in the literature. Comparing the calculated linewidth with the experimental linewidth, one can also obtain information about whether the spectra result from one or more than one active centre and the existence of disorder in the crystal field of the active centres.

1. Introduction

Trivalent-chromium-ion-doped crystals with a weak or intermediate crystal field are excellent materials for tunable solid state lasers. The laser performances of this kind of material depend on the spectroscopic properties such as the intensities and bandwidths of the absorption and the emission spectra as well as the lifetime of fluorescent states. All these properties are connected with the crystal-field effect and electron–phonon interaction, which is characterized by the crystal-field-splitting parameter $10Dq$, the effective phonon energy $\hbar\omega$ and the Huang–Rhys S -factor. A large number of papers studying the absorption and the emission spectra between 4A_2 and 4T_2 states in Cr^{3+} and calculating these parameters have been published [1–21]. In the analysis of this kind of spectra, many useful relations have been widely used. For example

$$10Dq = E_a({}^4A_2 \rightarrow {}^4T_2) \quad (1)$$

where E_a denotes the peak energy of the absorption spectrum. In the discussion of the Stokes shift E_S and the luminescence linewidth W , the following expressions have been widely adopted:

$$E_S = 2S\hbar\omega \quad (2)$$

$$W^2 = 8(\ln 2)S(\hbar\omega)^2 \coth(\hbar\omega/2kT). \quad (3)$$

However, all these discussions were based on a phenomenological single-mode model; the values of S and $\hbar\omega$ can only be estimated from other measurements and calculations, for

instance, measurement of the line shape of the spectrum and fitting it to a theoretical line-shape function or measurement of the linewidth variation versus temperature change and fitting it to the expressions such as equation (3). For calculations made in this way, the parameters obtained are somewhat like black-boxes; it is not evident whether they result from a single effect of one kind of Cr^{3+} centre or from a mixed effect of many kinds of Cr^{3+} centre. It would be beneficial if there was a way to correlate the luminescence linewidth as well as S and $\hbar\omega$ with the wavelengths of the peaks of the emission and the absorption spectra; even it is only an approximate method. We would like to establish one of these methods in the following paragraphs.

It should be pointed out that we are not going to study the microscopic mechanism in detail but we wish to find an approximate calculation method. Therefore, it can be said that the validity of the formulae introduced will mainly depend on whether they can give an answer in good agreement with experimental results.

2. Calculation formulae

By the point charge crystal-field approximation, the crystal-field-splitting parameter $10Dq$ was calculated to be [22]

$$10Dq = \frac{70}{42}(Ze^2\langle r^4 \rangle_{3d}/R^5) \quad (4)$$

where $-Ze$ is the point charge of the ligand and $\langle r^4 \rangle_{3d} = \int r^6 |\mathcal{R}_{3d}(r)|^2 dr$ with a radial wavefunction $\mathcal{R}_{3d}(r)$ for the Cr^{3+} 3d electron state. R denotes the distance between the centre of the chromium ion and the centre of the ligand. In the cases studied, the crystals have a melting point much higher than room temperature; the lattice vibrations at or below room temperature will have an amplitude δR at least two orders of magnitude smaller than those of R , i.e. $\delta R/R \leq 10^{-2}$. With reference to the work done by other researchers [23,24], it is reasonable to assume that Z and $\langle r^4 \rangle_{3d}$ are independent of R in the cases concerned. Therefore, in the following discussion, equation (4) can be written as

$$10Dq = AR^{-n} \quad (5)$$

where A is constant and $n = 5$ in the point-charge model. For a real crystal, the crystal-field effect on doped Cr^{3+} has contributions from many mechanisms besides the point charge Coulomb interaction; therefore, n can be assumed to have a different value from that in the point-charge model. From the experimental curve of reduced crystal-field splitting $10Dq$ versus the inverse of the reduced volume under up to 35 GPa pressure, Ducilos *et al* [23] obtained a value of n equal to 4.5 for $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ systems. It should be noted that their analysis shows that this n -value depends on the local compressibility of the Cr^{3+} sites; if this compressibility is high, then the n -value can be close to the point charge model value, i.e. n will be close to 5. This variation tendency perhaps corresponds to the fact that, the longer the distance of the active ion from the ligands, the more successful is the point charge model. The same chromium ions used as dopants in host crystals with different lattice constants will have different local compressibilities and so a different dependence of $10Dq$ on R (with different n -values). A larger lattice constant (larger R) corresponds to a higher local compressibility and so a higher n -value approaching 5. Therefore, within a certain limit, n is an increasing function of R . We assume that n/R is approximately a constant in the following discussion.

The single-configuration-coordinated model usually used in analyses of this kind of spectrum is in principle a 'breathing mode', i.e. a mode which belongs to A_{1g} symmetry.

On the basis of the previous discussion of the validity of equation (5), we assume in this paper that the expression for the Huang–Rhys S -factor introduced by Moreno *et al* [24], i.e.

$$S = n^2(10Dq)^2/2N\hbar MR^2\omega^3 \quad (6)$$

can be used to calculate the S -factor for the systems discussed in the configuration-coordinated model, with an effective phonon energy $\hbar\omega$ replacing the real A_{1g} -mode phonon energy. In equation (6), N is the ligand number of active ions and M the mass of the ligand; the interaction studied concentrated on complexes consisting of active ions and their nearest anions. We cannot employ this equation directly to calculate these parameters using data on only the absorption and the emission peak wavelengths. Changing the form of equation (6), we obtain

$$S\hbar\omega = (n^2\hbar^2/2NMR^2)(10Dq/\hbar\omega)^2. \quad (7)$$

Combining equation (7) with equations (1) and (2), then the phonon energy can be expressed as

$$\hbar\omega = E_a[n^2\hbar^2/NMR^2(E_a - E_e)]^{1/2} \quad (8)$$

and the linewidth of the emission 4T_2 to 4A_2 will become

$$W = [2.7725(E_a - E_e)\hbar\omega \coth(\hbar\omega/2kT)]^{1/2} \quad (9)$$

where E_e is the peak energy of emission spectrum. M can be taken as $M_o = 2.7 \times 10^{23}$ g for oxides and $M_f = 3.2 \times 10^{-23}$ g for fluorides. Referring to [23], we can take $n = 4.5$ and an approximate value of R equal to 2×10^{-8} cm and then obtain $n/R = 2.25 \times 10^8$ cm for ruby. As pointed out previously, for all the tunable oxide and fluoride laser crystals, one can assume the same value for n/R . After substituting all the physical quantities and $N = 6$ into equation (8) and expressing the energy of the phonon in the units of wavenumber (reciprocal centimetres) the following equations resulted:

$$\hbar\omega \simeq 2.25E_a[0.3456/(E_a - E_e)]^{1/2} \quad (10)$$

for oxides, and

$$\hbar\omega \simeq 2.25E_a[0.2910/(E_a - E_e)]^{1/2} \quad (11)$$

for fluorides.

Using equations (10) or (11), the effective phonon energy can be calculated; then the linewidth W and the Huang–Rhys S -factor can be obtained from equations (9) and (2).

3. Results and analyses

The linewidths of the emission 4T_2 to 4A_2 of the chromium ions in different hosts have been calculated and compared with data obtained by emission spectra published in literature. All the results are listed in tables 1 and 2. It can be seen that the percentage deviations of the calculation are smaller than 10%, except in special cases, which either have disorders of the crystal field at Cr^{3+} centres or present a different kind of chromium centre. In these cases, the calculated linewidths are much smaller than those obtained from experimental results as can be expected in principle. The case of $Mg_2SiO_4:Cr^{3+}$ is worth mentioning; the fact that

Table 1. Comparison of calculated linewidths for ${}^4T_2 \rightarrow {}^4A_2$ emission of Cr^{3+} ions in oxides with related experimental results.

Crystal	T (K)	E_a (cm^{-1})	E_c (cm^{-1})	Calculated W (cm^{-1})	Experimental results		Deviation (%)
					W (cm^{-1})	References	
$Al_2(WO_4)_2$	300	15 229	12 157	2073	2100	[1, 3]	1.3
$ZnWO_4$	300	13 666	10 278	2117	2105	[21]	0.6
$ZnWO_4$	9	13 500	10 145	1693	1588	[6]	6.6
$YAl_3(BO_3)_4$	300	16 949	13 513	2215	2127	[4]	4.1
$La_3Ga_5SiO_4$	300	15 748	σ :11 395	2406	2437	[5]	1.3
	300	15 748	π :11 549	2370	2525	[5]	6.1
YGG	300	16 293	13 691	1971	1900	[2]	1.5
GGG	300	15 963	13 617	1886	1900	[2]	0.7
YSGG	300	16 128	13 332	2022	2100	[2]	3.7
LGG	300	14 794	11 758	2051	2100	[2]	2.3
GSGG	300	15 631	12 993	1963	2000	[2]	1.9
	177	15 430	13 506	1606	1558	[17, 18]	3.1
	89	15 430	13 624	1538	1429	[17, 18]	7.6
GAGG	300	15 600	13 444	1817	1732	[17, 18]	4.9
	100	15 600	13 717	1576	1514	[17, 18]	4.1
$La_3Ga_5GeO_{14}$	300	15 385	10 417	2537	2620	[19]	3.2
$La_3Ga_{3.5}Nb_{0.5}O_{14}$	300	15 152	9709	2634	2825	[19]	6.8
$La_3Ga_{3.5}Ta_{0.5}O_{14}$	300	15 038	9709	2607	2875	[19]	9.3
Mg_2SiO_4	290	14 900 ^a	13 308	1596	1513	[15, 16]	5.5
GGG (Ca, Mg, Zr)	300	15 630	12 926	1946	1909	[11]	1.9
$LiTaO_3$	300	15 543	10 538	2015	2140	[12]	5.8
MgO	300	16 188	12 671	1878	1746	[12, 13]	7.0
$Ca_3Ga_2Ge_4O_{14}$	300	16 000	10 989	2560	3645	[19]	29.7 ^b
$Sr_3Ga_2Ge_4O_{14}$	300	16 260	11 905	2420	4085	[19]	40.8 ^b
Sc_2O_3	14	15 200	11 875	1792	2329	[10]	23.0 ^c

^a Low-field value of $10Dq$ was used.

^b Disorder of the crystal field at Cr^{3+} .

^c Presence of a second Cr^{3+} site.

the linewidth of 4T_2 emission calculated from equations (7) and (8) using a low-field $10Dq$ -value [15] agreed well with the experimental result at 290 K [16] shows that the 4T_2 broad-band emission is produced by low-field Cr^{3+} centres in mirror symmetry. This conclusion is in agreement with that obtained in [15]. At a low temperature $T = 10$ K, the fluorescence of Cr^{4+} in the Mg_2SiO_4 crystal is very strong and it appears at a wavelength close to that of the 4T_2 broad-band emission produced by Cr^{3+} ; so the linewidth calculated for 4T_2 emission at $T = 10$ K by the method introduced is much smaller than the experimental value obtained from the spectrum shown in figure 4 of [15]. General speaking, the fact that the calculated linewidths at different temperatures are in good agreement with experimental results means that the S -factor and $\hbar\omega$ -value calculated in this way are reasonable. The results for four fluorides obtained from equations (7) and (10) are shown in table 3; they agree very well with those obtained by other workers using the traditional method. In particular, for the case of $ScF_3:Cr^{3+}$, the values of S and $\hbar\omega$ obtained by Huber *et al* [10] using a Pekarian fit to the emission line shape were 3.0 and 380 cm^{-1} ; the corresponding results of the calculation in this paper are 3.0 and 367 cm^{-1} , respectively. The agreement is very good. It should be

noted that the formula introduced by Moreno *et al* [24] was used in a different way from their original use. Calculating in this way, we can obtain the S -factor, $\hbar\omega$ and linewidth W at the same time without measuring $\hbar\omega$ by another experimental method and the results are in better agreement with those obtained by the more complicated calculation method and experimental data.

Table 2. Comparison of calculated linewidths for ${}^4T_2 \rightarrow {}^4A_2$ emission of Cr³⁺ ions in fluorides with related experimental results.

Crystal	T (K)	E_a (cm ⁻¹)	E_c (cm ⁻¹)	Calculated W (cm ⁻¹)	Experimental results		Deviation (%)
					W (cm ⁻¹)	Reference	
LiSrAlF ₆	20	15 676	12 821	1679	1699	[7]	1.2
LiSrGaF ₆	295	15 873	12 054	2237	2438	[9]	8.2
Na ₃ Ga ₂ Li ₃ F ₁₂	18	16 069	13 313	1685	1740	[8]	3.2
ScF ₃	14	14 280	12 028	1510	1495	[10]	1.0
KZnF ₃	80	14 858	12 934	1482	1521	[19]	2.6

Table 3. Comparison of calculated Huang–Rhys S -factors and phonon energy $\hbar\omega$ of ${}^4T_2 \rightarrow {}^4A_2$ emission of Cr³⁺ with those obtained by traditional method.

Crystal	T (K)	E_a (cm ⁻¹)	E_c (cm ⁻¹)	This method		Other method		Reference
				S	$\hbar\omega$ (cm ⁻¹)	S	$\hbar\omega$ (cm ⁻¹)	
K ₂ NaScF ₆	295	15 600	13 100	3.30	379	3.95	380	[14]
K ₂ NaGaF ₆	295	16 000	13 600	3.03	396	3.98	378	[14]
Na ₃ Ga ₂ Li ₃ F ₁₂	18	16 069	13 313	3.7	372	3.5	400	[8]
ScF ₃	14	14 280	12 028	3.0	367	3.0	380	[10]

4. Discussion

First it should be emphasized that the method introduced is really useful because it can be used not only to calculate W , S and $\hbar\omega$ simply by measuring the wavelengths of the absorption and the emission peaks, but also, more importantly, to judge whether there is any disorder of the crystal field or whether different chromium centres exist and to determine which centre is responsible for the emission observed. We could not find a similar method in the literature. In the process of introducing the main calculation formulae, several assumptions and approximations have been made. Their validity can be justified by the comparison between the calculated results and the experimental data. In any case, we would not insist on the correctness of each step to obtain the final calculation formulae. We believe that, in judging the validity of these kinds of approximation method, the main criterion should be to see whether it can give us any new information and a satisfactory explanation of experimental facts. Because the work of Moreno *et al* [24] has been used as an intermediate step to establish the correlation between related experimental parameters, we would like to say a few words about that. At first sight the validity of their formulae does not seem to be believable, because the results that they obtained did not agree well with the experimental data as can be seen from table 1 in [24]. In fact, by means of the original formulae, in order to obtain Huang–Rhys S -factor, the exponent n value should

be calculated by a certain theoretical method; also the ω -value has to be taken from other experiments. Different approximation methods can give various values for n differing from each other by up to 44% for the same system. It can be considered that the differences between the calculated and experimental values of S resulted mainly from the theoretical calculation of n . Although their idea is correct, the real significance of it seems to be lost in a 'theoretical fog'. The calculations in this paper can be seen as a justification of their work, but the problem of obtaining an accurate value for n by theoretical calculation has been avoided and all the results can be directly compared with experimental data without being affected by the accuracy of the theoretical method.

In conclusion we would like to admit that this work is still of a preliminary nature. One aim of publishing it is to stimulate a detailed discussion and to further a more complete research of its theoretical bases, practical meanings and limitations. The calculation for Cr^{3+} -doped chlorides has not been included mainly because we cannot collect enough spectral data for these samples.

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