

The Huang-Rhys factor $S(a_{1g})$ for transition-metal impurities: a microscopic insight

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1992 J. Phys.: Condens. Matter 4 9481

(<http://iopscience.iop.org/0953-8984/4/47/027>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.159

The article was downloaded on 12/05/2010 at 12:35

Please note that [terms and conditions apply](#).

The Huang–Rhys factor $S(a_{1g})$ for transition-metal impurities: a microscopic insight

M Moreno†, M T Barriuso‡ and J A Aramburu†

† Sección Ciencia de Materiales, DCITYM, Facultad de Ciencias, Universidad de Cantabria, 39005 Santander, Spain

‡ Departamento de Física Moderna, Facultad de Ciencias, Universidad de Cantabria, 39005 Santander, Spain

Received 10 June 1992, in final form 18 August 1992

Abstract. A microscopic model for evaluating the Huang–Rhys factor $S(a_{1g})$ associated with the symmetric mode of a transition-metal impurity M in insulators is proposed. It is applied to the first excited states of Cr^{3+} , V^{2+} , Mn^{2+} and Cu^{2+} . If $10Dq$ is proportional to R^{-n} (R is the metal–ligand distance) it is shown that $S(a_{1g})$ is proportional to n^2 as well as to $[\omega(a_{1g})]^{-3}$. Theoretical calculated values of the exponent n indicate that it varies slightly along the ligand series $\text{F}^- \rightarrow \text{Cl}^- \rightarrow \text{Br}^-$ giving rise to an increase in $S(a_{1g})$. This explains why the Stokes shift of systems involving MBr_N units can be similar or higher than the corresponding shifts of MF_N complexes. The calculated values of $S(a_{1g})$ are reasonably close to available experimental estimations and support the fact that the contribution of the a_{1g} mode to the Stokes shift is between 50 and 70% for CrX_6^{3-} ($X \equiv$ halides) complexes while it is smaller than 40% for the corresponding systems involving Mn^{2+} . The dependence of $S(a_{1g})$ on R is also analysed, leading to an increase in $S(a_{1g})$ upon increasing R . This trend which has been directly verified for V^{2+} in chlorides can also explain the increase in the Stokes shift observed experimentally when R is increased.

1. Introduction

Salient features displayed by optical properties associated with localized centres in non-metallic materials arise from electron–phonon coupling. Examples of these are the Stokes shift, the appearance of vibrational progressions in optical spectra and the existence of non-radiative transitions [1].

The strength of the linear electron–phonon coupling between an electronic excited state Γ_e and a vibrational mode Γ_i (whose frequency is $\omega_i/2\pi$) is measured through the so-called Huang–Rhys factor S_i . This factor alone determines the relative intensity of a given member corresponding to the progression due to the Γ_i mode. The Huang–Rhys factor S_i is zero if $\Gamma_i \not\subset \Gamma_e \times \Gamma_e$ and so, if the localized system is centrosymmetric, only progressions with even vibrational modes are allowed.

As regards the Stokes shift ΔE_s^0 , for an electric dipole transition it is given by [2]

$$\Delta E_s^0 = 2 \sum_i S_i \hbar \omega_i \quad (1)$$

and thus involves the coupling to all allowed vibrational modes. In (1), ΔE_s^0 is thus taken as the difference between the first moments M_1 of the absorption and the

corresponding emission band. If the transition is, however, parity forbidden but assisted by an odd vibration mode whose frequency is $\omega_u/2\pi$, (1) has to be replaced by

$$\Delta E_s = \Delta E_s^0 + 2\hbar\omega_u \tanh(\hbar\omega_u/2kT). \quad (2)$$

As $\hbar\omega_u$ is typically of the order of 100 cm^{-1} , the difference between ΔE_s and ΔE_s^0 becomes equal to $2\hbar\omega_u$ at low temperatures but may be negligible at room temperature.

In the case of transition-metal (TM) impurities M in O_h or D_{4h} symmetries the so-called crystal-field transitions are magnetic dipole allowed giving rise to weak zero-phonon lines of energy E_{ZPL} . The assistance of an odd mode gives rise to a more intense false origin of the progressions located at $E_{ZPL} + \hbar\omega_u$ for absorption peaks at low temperatures. Furthermore, associated with the false origin, several progressions involving local even modes of the MX_N complex (formed with the X ligands) have been discovered. In particular for TM impurities in O_h symmetry, clear evidence of the coupling to the a_{1g} as well as to the e_g Jahn-Teller mode has been obtained for several cases. Good examples have been found for instance for Cr^{3+} in some elpasolite lattices [3-7]. This experimental finding is thus quite consistent with the good understanding of optical and EPR parameters due to TM impurities in insulators reached only on the basis of localized MX_n unit [8].

Despite the relevant role played by the Huang-Rhys factors S_i , few efforts have been devoted to gaining a better microscopic insight into them. Through this work a model for calculating $S(a_{1g})$ is developed and applied to the first excited state (${}^4T_{2g}$ or ${}^4T_{1g}$) of some d^3 [4, 5, 7, 9] and d^5 [10-12] O_h complexes, as well as to the ${}^2B_{2g}$ ($\sim xy$) state of the D_{4h} $CuCl_4^{2-}$ complex [13].

If we designate by E the energy difference between the excited and the ground state a microscopic insight into $S(a_{1g})$ requires us to know the dependence of E upon the metal-ligand distance R . In the case of the d^3 systems referred to, the relative position of the ${}^4T_{2g}$ state is fixed only by $10Dq$. A similar situation holds for the ${}^2B_{2g}$ state of $CuCl_4^{2-}$. As regards the ${}^4T_{1g}$ state of d^5 impurities with local O_h geometry it depends on $10Dq$ as well as on the effective Racah parameters B and C .

Work performed on several fluoride complexes [10, 14, 15] indicates, however, that B and C are almost independent of R . Furthermore, designating by R_{ML} the metal-ligand distance expected on the basis of ionic radii, it is found that in the vicinity of R_{ML} ($\delta R/R_{ML} \leq 10^{-2}$) the dependence of $10Dq$ upon R can be represented by the law [10, 14, 15]

$$10Dq = AR^{-n}. \quad (3)$$

A law of this kind with $n = 5$ is reached within the framework of crystal-field theory which gives rise, however, to $10Dq$ -values substantially smaller than experimental data. Values of $10Dq$ comparable with experimental data are obtained within the more realistic molecular orbital scheme applied to the MX_N complex [8].

As the exponent n is strongly related to $S(a_{1g})$, we have firstly performed theoretical calculations of it for several TM complexes in order to explore its dependence on the ligand nature and the kind of impurity. In a second step we have evaluated $S(a_{1g})$ for several impurities (using for this goal the $\omega(a_{1g})$ -value measured experimentally) and compared our results with available experimental estimations of $S(a_{1g})$. In fact, precise determinations of $S(a_{1g})$ for TM impurities with O_h geometry are often difficult as several progressions exist in the same spectrum with overlaps between them and thus

precise values of relative intensities associated with each peak of a given progression cannot be obtained.

Aside from the understanding of the experimental $S(a_{1g})$ -values through the present research we wish to investigate the following points:

(1) the contribution of

$$\Delta E_s^0(a_{1g}) = 2S(a_{1g})\hbar\omega(a_{1g}) \quad (4)$$

to the Stokes shift ΔE_s ;

(2) the dependence of $S(a_{1g})$ upon the ligand nature provided that both the impurity and the local geometry are kept (in this case we shall explore whether the trends predicted for $\Delta E_s^0(a_{1g})$ are followed or not by ΔE_s);

(3) the dependence of $S(a_{1g})$ upon the metal–ligand distance R .

2. Theoretical details

Within the linear electron–phonon coupling scheme the Huang–Rhys factor associated with a single vibrational mode Γ_i (whose collective coordinate is Q_i) and an electronic state Γ_e is given by [1, 2]

$$S_i = (2\hbar K_i \omega_i)^{-1} (\partial E / \partial Q_i)^2 \quad (5)$$

where K_i is the force constant of the mode. For an MX_N complex whose ligands are all equivalent, $Q(a_{1g})$ is just given by

$$Q(a_{1g}) = \sqrt{N}(R - R_0) \quad (6)$$

where R_0 denotes the equilibrium metal–ligand distance in the ground state depending upon the chemical pressure exerted by the rest of the lattice as well as on external applied pressures. In all cases studied in this work, $\partial E / \partial R$ is essentially given by $\partial(10Dq) / \partial R$ [1]. Thus taking into account equation (3) and putting $K(a_{1g}) = M\omega^2(a_{1g})$, where M is the ligand mass, we find that

$$S(a_{1g}) = n^2(10Dq)^2 / 2N\hbar M R_0^2 \omega^3(a_{1g}). \quad (7)$$

In this expression, $10Dq$ and $\omega(a_{1g})$ both depend on the actual R_0 -value.

As few measurements of the exponent n are available in the literature [10, 16–18] we have calculated it for some complexes using the self-consistent charge extended Hückel (SCCEH) and MS X_α methods. Details of the calculation procedure are given for instance in [19]. The results of our calculations are collected in table 1 together with theoretical values of the exponent n found by other workers [14, 15, 20, 21].

3. Applications and discussion

Inspection of table 1 tells us that the HFR and SCCEH methods give values of n which lie between 4 and 6 while the corresponding values obtained by X_α -type methods are, however, systematically smaller. A salient feature of table 1 is the near independence of the exponent n on the ligand nature as inferred from comparing the values found for MnF_6^{4-} and MnCl_6^{4-} or those for CuF_4^{2-} , CuCl_4^{2-} and CuBr_4^{2-} .

As regards the comparison with available experimental measurements an n -value of 4.7 has been derived for MnF_6^{4-} by analysing the variation in the optical spectrum

Table 1. Theoretical values of the exponent n (defined in (3)) found for different complexes using Hartree-Fock-Roothaan (HFR), SCC EH or X_α -type methods.

Complex	Geometry	Calculation method	n	Reference
CrF_6^{3-}	O_h	HFR	4.3	[14]
CrF_6^{3-}	O_h	HFR	5.9	[14]
VF_6^{4-}	O_h	HFR	5.2	[14]
MnF_6^{4-}	O_h	SCC EH	6.1	Present work
		MS X_α	4.8	Present work
		HFR	5.5	[15]
		DV X_α	3.4	[19]
MnF_8^{6-}	O_h	SCC EH	5.9	Present work
MnCl_6^{4-}	O_h	SCC EH	5.8	Present work
MnS_4^{4-}	T_d	HFR	5.5	[20]
NiF_4^{3-}	D_{4h}	SCC EH	5.5	Present work
		MS X_α	3.9	Present work
CuF_4^{2-}	D_{4h}	SCC EH	5.0	Present work
		MS X_α	3.2	Present work
CuCl_4^{2-}	D_{4h}	SCC EH	5.0	Present work
		MS X_α	3.3	Present work
CuBr_4^{2-}	D_{4h}	MS X_α	3.4	Present work
CuF_6^{4-}	D_{4h}^a	SCC EH	4.7	Present work
		MS X_α	4.1	Present work
CuCl_6^{4-}	D_{4h}^a	SCC EH	4.3	Present work
		MS X_α	3.2	Present work

^a 'Elongated octahedral' geometry where the four equatorial ligands are closer to the central cation than the two axial ligands are.

through the series of fluoroperovskites doped with Mn^{2+} [10, 18]. In the case of NiO [16] and $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ [17] n values of 5 and 4.5, respectively, have been obtained through the variations induced in the optical spectrum by hydrostatic pressures. In the latter case an n -value of 4.5 was derived, however, assuming that the local compressibility is equal to the bulk compressibility.

Bearing in mind all these facts, we have calculated the $S(a_{1g})$ -values collected in table 2 assuming that, as a reasonable first approximation, $n = 5$ and taking $\omega(a_{1g})$ -values from experiment. It is worth noting that, although the n -value of 5 is obtained in a pure crystal-field theory, this has to be viewed as a fortuitous coincidence. In fact, crystal-field theory predicts $10Dq$ -values which are much smaller than experimental data [8].

Let us firstly discuss the $b_{2g}(\sim xy) \rightarrow b_{1g}(\sim x^2 - y^2)$ transition of the square-planar CuCl_4^{2-} unit where only the a_{1g} vibration of the complex can give rise to progressions, as is indeed observed [13]. From the analysis of the intensity of nine peaks resolved at 10 K an $S(a_{1g})$ -value of 3.7 has been derived [13] which is close to our calculated value. In $(\text{MetH})_2\text{CuCl}_4$, however, no luminescence has been reported which prevents the comparison of the Stokes shift with our calculated $\Delta E_s^0(a_{1g})$ -value.

In all other systems included in table 2, luminescence has been observed although vibrational progressions exhibit a more complex pattern. This means that there is a possibility of coupling to other even modes (and especially to the e_g Jahn-Teller mode of the octahedral complex) as well as the possibility of the existence of several false origins.

Table 1. Calculated values of $S(a_{1g})$ and $\Delta E_s^0(a_{1g})$ using equation (7), assuming $n = 5$ and taking $\omega(a_{1g})$ and $10Dq$ from experiment. The values of available experimental Stokes shifts (measured at the temperatures indicated in parentheses) and $S(a_{1g})$ are also given. With the exception of $(\text{MeH})_2\text{CuCl}_4$ where the CuCl_4^{2-} complex is D_{4h} square planar, in all other systems the complex exhibits a local octahedral geometry.

System	$S(a_{1g})$						Reference	
	r_0 (Å)	$\hbar\omega(a_{1g})$ (cm^{-1})	$10Dq$ (cm^{-1})	Calculated	Experimental	$\Delta E_s^0(a_{1g})$ (cm^{-1})		ΔE_s (cm^{-1})
$(\text{MeH})_2\text{CuCl}_4$	2.26	275	12480	4.3	3.7	2365	—	[13]
$\text{Rb}_2\text{KGaF}_6:\text{Cr}^{3+}$	556	15970	1.4	—	1550	1460 (RT)	[7]	[4, 5]
$\text{Cs}_2\text{NaInCl}_6:\text{Cr}^{3+}$	2.45	298	13000	2.1	1.6	1250	1780 (15 K)	[5]
$\text{Cs}_2\text{NaYBr}_6:\text{Cr}^{3+}$	2.60	183	12400	3.2	—	1170	2200 (15 K)	[9]
$\text{MgCl}_2:\text{V}^{2+}$	2.50	240	9330	2.0	4	960	1910 (10 K)	[9]
$\text{CdCl}_2:\text{V}^{2+}$	2.52	220	9000	2.4	4.5	1060	2250 (10 K)	[9]
$\text{KZnF}_3:\text{Mn}^{2+}$	2.08	540	8220	0.4	—	390	1350 (RT)	[10, 12]
MnCl_2	2.61	234	6700	1.0	2.4	470	2936 (70 K)	[11]

Comparing our calculated values of $\Delta E_s^0(a_{1g})$ with the corresponding Stokes shifts ΔE_s found experimentally, we note that $\Delta E_s^0(a_{1g}) < \Delta E_s$ as it should in view of (2).

In the case of Cr^{3+} systems with ${}^4T_{2g}$ as the first excited state, we see that our calculated $S(a_{1g})$ -value of 2.1 for $\text{CsNaInCl}_6:\text{Cr}^{3+}$ is reasonably close to the experimental estimation of $S(a_{1g}) = 1.6$. Furthermore our results indicate that the contribution of $\Delta E_s^0(a_{1g})$ to the Stokes shift ΔE_s lies between 50 and 70%. This concurs with the experimental finding for $\text{CsNaInCl}_6:\text{Cr}^{3+}$ where it has been found [4, 5] that ΔE_s^0 is essentially given by

$$\Delta E_s^0 = \Delta E_s^0(a_{1g}) + \Delta E_s^0(e_g) \quad (8)$$

and $\Delta E_s^0(a_{1g}) = 955 \text{ cm}^{-1}$ and $\Delta E_s^0(e_g) = 625 \text{ cm}^{-1}$.

As regards $\text{MgCl}_2:\text{V}^{2+}$ our calculated value $S(a_{1g}) = 2.0$ is smaller than $S(a_{1g}) = 4.0$ estimated [9] from the relative intensity of first peaks of the corresponding progression. We believe, however, that the latter value is an overestimation as, if $S(a_{1g}) = 4$, then $\Delta E_s^0(a_{1g}) = 1920 \text{ cm}^{-1}$ which is almost equal to the Stokes shift measured at 10 K, thus implying that no progressions associated with the e_g Jahn-Teller mode of VCl_6^{4-} exist. Nevertheless Galli *et al* [9] observe such progressions, estimating that $S(e_g) = 1.0$. Therefore, taking into account equations (2) and (8) and the reported values $S(e_g) = 1.0$, $\hbar\omega(e_g) = 209 \text{ cm}^{-1}$ and $\Delta E_s = 1910 \text{ cm}^{-1}$ at 10 K we find that $\Delta E_s^0(e_g) = 420 \text{ cm}^{-1}$ and thus $\Delta E_s^0(a_{1g}) < 1490 \text{ cm}^{-1}$ and $S(a_{1g}) < 3.1$. The latter value is now more compatible with $S(a_{1g}) = 2.0$ calculated under the assumption that $n = 5$.

Concerning $\text{KZnF}_3:\text{Mn}^{2+}$ the inspection of the luminescence spectrum obtained by Rodríguez *et al* [12] indicates that $S(a_{1g})$ is likely to be smaller than unity although an estimation of it has not been reported. Nevertheless $\Delta E_s^0(a_{1g})$ can be determined indirectly from the experimental value $\Delta E_s = 1350 \text{ cm}^{-1}$ measured at room temperature and use of (8). The $\Delta E_s^0(e_g)$ -value of 900 cm^{-1} is obtained from $S(e_g) = 1.5$ measured experimentally [12] through the reduction in the spin-orbit coupling coefficient due to the Ham effect. A similar value was found for RbMnF_3 [22]. Thus, if we take into account equation (8), a $\Delta E_s^0(a_{1g})$ -value of 450 cm^{-1} is derived which is not far from the calculated value in table 2.

All this then support the fact that at variance with findings for d^3 systems, $S(e_g)$ for MnF_6^{4-} can be a factor of about 3 higher than $S(a_{1g})$. A similar situation would arise for MnCl_2 where indirect estimations by Ronda *et al* [11] lead to $S(e_g)/S(a_{1g}) = 4.9$.

As regards the dependence of $S(a_{1g})$ upon the ligand nature, table 2 shows that, for Cr^{3+} and Mn^{2+} complexes, $S(a_{1g})$ increases when we go through the ligand series $\text{F}^- \rightarrow \text{Cl}^- \rightarrow \text{Br}^-$. Taking into account (5) and (7), now we can say that this increase is due to the significant decrease in both the force constant $K(a_{1g})$ and $\omega(a_{1g})$ on going through the series, which is not balanced by the decrease experienced by $(10Dq)^2$ and R_0^{-2} . In fact the relative values of $K(a_{1g})$, $\omega(a_{1g})$ and $10Dq$ through the series of complexes $\text{MF}_6 \rightarrow \text{MCl}_6 \rightarrow \text{MBr}_6$ are roughly as follows [23, 24]:

$K(a_{1g}) = 1$	$\omega(a_{1g}) = 1$	$10Dq = 1$	for F^-
$K(a_{1g}) = 0.60$	$\omega(a_{1g}) = 0.55$	$10Dq = 0.87$	for Cl^-
$K(a_{1g}) = 0.48$	$\omega(a_{1g}) = 0.35$	$10Dq = 0.80$	for Br^- .

Therefore the increase experienced by $S(a_{1g})$ along the ligand series permits one to understand why the Stokes shift for $\text{Cs}_2\text{NaYBr}_6:\text{Cr}^{3+}$ is close to that for $\text{Rb}_2\text{KGaF}_6:\text{Cr}^{3+}$ although local stretching frequencies for the former are about one third of those for the latter.

Let us now briefly discuss the dependence of $S(a_{1g})$ upon R_0 for a given complex which can be experimentally measured either by changing the host lattice or by applying an external hydrostatic pressure. The dependence of $\omega(a_{1g})$ upon R_0 follows the Grüneisen relation

$$\partial(\ln \omega) / \partial(\ln R_0) = -3\gamma. \quad (9)$$

Therefore taking into account equations (3), (7) and (9) we finally obtain

$$S(a_{1g}) \propto R_0^{9\gamma - 2(n+1)}. \quad (10)$$

As the Grüneisen coefficient γ for stretching modes is positive and normally lies between 2 and 3 [25, 26] we expect that, if $n \simeq 5$, then the exponent $9\gamma - 2(n + 1)$ in (10) is clearly positive and so $S(a_{1g})$ should increase upon increasing the metal-ligand distance R_0 . This conclusion is well supported by experimental data on $\text{MgCl}_2:\text{V}^{2+}$ and $\text{CdCl}_2:\text{V}^{2+}$ gathered in table 2. In fact, $\text{MgCl}_2:\text{V}^{2+}$ exhibits a $10Dq$ -value which is 330 cm^{-1} higher than that of $\text{CdCl}_2:\text{V}^{2+}$. Following equation (3) and taking $n = 5$, such a difference would correspond to $\Delta R_0 \simeq 0.02 \text{ \AA}$ between the R_0 -values for $\text{CdCl}_2:\text{V}^{2+}$ and $\text{MgCl}_2:\text{V}^{2+}$. This is quite consistent with findings for substitutional impurities placed in a series of similar lattices where R_0 -values are normally ordered as the corresponding values R_p of the perfect lattice [8]. Furthermore this idea is reinforced by the smaller $\hbar\omega(a_{1g})$ -value of 220 cm^{-1} shown by $\text{CdCl}_2:\text{V}^{2+}$ compared with $\hbar\omega(a_{1g}) = 240 \text{ cm}^{-1}$ for $\text{MgCl}_2:\text{V}^{2+}$. The difference $\hbar\Delta\omega(a_{1g}) = -20 \text{ cm}^{-1}$ between them is compatible with (9), $\gamma \simeq 3$ and again $\Delta R_0 \simeq 0.02 \text{ \AA}$. Our calculated values give a ratio of $S(a_{1g})$ for $\text{CdCl}_2:\text{V}^{2+}$ to $S(a_{1g})$ for $\text{MgCl}_2:\text{V}^{2+}$ equal to 1.2, which compares well with the experimental estimation (table 2). Furthermore in these cases an increase in $S(e_g)$ upon increasing R_0 has also been reported by Galli *et al* [9] who find that $S(e_g) = 1.7$ for $\text{CdCl}_2:\text{V}^{2+}$ while $S(e_g) = 1.0$ for $\text{MgCl}_2:\text{V}^{2+}$.

It is worth noting that the dependence of Huang-Rhys factors upon R_0 could also give rise to an increase in ΔE_s^0 as the metal-ligand distance is increased. In fact as regards the dependence of $\Delta E_s^0(a_{1g})$ upon R_0 it is given by

$$\Delta E_s^0(a_{1g}) \propto R_0^{6\gamma - 2(n+1)}. \quad (11)$$

Considering again the two systems in table 2 involving VCl_6^{4-} units and assuming that $\gamma = 3$ and $n = 5$, we find that $\Delta E_s^0(a_{1g}) \propto R_0^6$. This result is thus compatible with the experimental increase $\delta(\Delta E_s) = 340 \text{ cm}^{-1}$ on going from $\text{MgCl}_2:\text{V}^{2+}$ to $\text{CdCl}_2:\text{V}^{2+}$ although the calculated $\delta[\Delta E_s^0(a_{1g})]$ -value is only 100 cm^{-1} . Furthermore, taking into account the estimated values of $S(e_g)$ as well as $\hbar\omega(e_g) = 209 \text{ cm}^{-1}$ for $\text{MgCl}_2:\text{V}^{2+}$ and $\hbar\omega(e_g) = 185 \text{ cm}^{-1}$ for $\text{CdCl}_2:\text{V}^{2+}$, we find that $\delta[\Delta E_s^0(e_g)] = 210 \text{ cm}^{-1}$; so the experimental increase $\delta(\Delta E_s) = 340 \text{ cm}^{-1}$ can reasonably be understood.

In the case of Mn^{2+} -doped fluoroperovskites it has been observed [10] that, at room temperature, $\Delta E_s = 1675 \text{ cm}^{-1}$ for $\text{RbCdF}_3:\text{Mn}^{2+}$ which is 320 cm^{-1} higher than the value in table 2 for $\text{KZnF}_3:\text{Mn}^{2+}$. Therefore, as the metal-ligand distances $R_0 = 2.13 \text{ \AA}$ for $\text{RbCdF}_3:\text{Mn}^{2+}$ and $R_0 = 2.08 \text{ \AA}$ for $\text{KZnF}_3:\text{Mn}^{2+}$ have been derived by

three independent methods [10, 27] a similar situation to that observed for V^{2+} chlorides is again encountered. Therefore, for MnF_6^{4-} in fluoroperovskites, $S(a_{1g})$ would also increase as R_0 increases.

Although the results reported here are encouraging, further efforts are necessary for a better understanding of electron-phonon coupling in TM impurities. The achievement of precise values of the exponent n , the calculation of the Huang-Rhys factor of the Jahn-Teller mode e_g and the extension of the analysis carried out in this work to a larger number of systems are among the goals for the near future.

Acknowledgments

Useful discussions with Dr F Rodríguez on the luminescence of MnF_6^{4-} complexes are acknowledged. This work has been supported by Comisión Interministerial de Ciencia y Tecnología under project MAT90-0668.

References

- [1] Henderson B and Imbusch G F 1989 *Optical Spectroscopy of Inorganic Solids* (Oxford: Clarendon) ch 5 and 6
- [2] Bourgoin J and Lanno M 1983 *Point Defects in Semiconductors II* (Berlin: Springer) p 106
- [3] Ferguson J, Guggenheim H J and Wood D L 1971 *J. Chem. Phys.* **54** 504
- [4] Gudel H U and Snellgrove T R 1978 *Inorg. Chem.* **17** 1617
- [5] Knochenmuss R, Reber C, Rajasekharan M V and Gudel H U 1986 *J. Chem. Phys.* **85** 4280
- [6] Dolan J F, Kappers L A and Bartram R H 1986 *Phys. Rev. B* **33** 7339
- [7] Marco de Lucas C, Rodríguez F, Dance J M, Moreno M and Tressaud A 1991 *J. Lumin.* **48-9** 835
- [8] Moreno M 1990 *J. Phys. Chem. Solids* **51** 835, and references therein
- [9] Galli B, Hauser A and Gudel H U 1985 *Inorg. Chem.* **24** 2271
- [10] Rodríguez F and Moreno M 1986 *J. Chem. Phys.* **84** 692
- [11] Ronda C R, Siekman H H and Haas C 1987 *Physica B* **144** 331
- [12] Rodríguez F, Riesen H and Gudel H U 1991 *J. Lumin.* **50** 101
- [13] McDonald R G and Hitchman M A 1986 *Inorg. Chem.* **25** 3273
- [14] Francisco E, Florez M, Barandiarán Z, Fernández Rodrigo G, Luaña V, Recio J M, Bermejo M, Seijo L and Pucyo L 1987 *Cryst. Latt. Defects Amorph. Mater.* **15** 45
- [15] Luaña V, Bermejo M, Florez M, Recio J M and Pucyo L 1989 *J. Chem. Phys.* **90** 6409
- [16] Drickamer H 1967 *J. Chem. Phys.* **47** 1880
- [17] Duclos S J, Vohra Y K and Ruoff A L 1990 *Phys. Rev. B* **41** 5372
- [18] Rodríguez F, Moreno M, Tressaud A and Chaminade J P 1987 *Cryst. Latt. Defects Amorph. Mater.* **16** 221
- [19] Barriuso M T, Aramburu J A and Moreno M 1990 *J. Phys.: Condens. Matter* **2** 771
- [20] Adachi H, Shiokawa S, Tsukada M, Satoko C and Sugano S 1979 *J. Phys. Soc. Japan* **47** 1528
- [21] Richardson J W and Janssen G J M 1989 *Phys. Rev. B* **39** 4958
- [22] Solomon E I and McClure D S 1974 *Phys. Rev. B* **9** 4690
- [23] Nakamoto K 1986 *Infrared and Raman Spectra of Inorganic and Coordination Compounds* 4th edn (New York: Wiley) p 153
- [24] Jorgensen C K 1971 *Modern Aspects of Ligand Field Theory* (Amsterdam: North-Holland) p 347
- [25] Brüesch P 1982 *Phonons: Theory and Experiments I* (Berlin: Springer) p 174
- [26] Breñosa A G, Moreno M, Rodríguez F and Couzi M 1991 *Phys. Rev. B* **44** 9859
- [27] Barriuso M T and Moreno M 1984 *Phys. Rev. B* **29** 3623