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Abstract. Pb$^+$(1) centres in alkaline-earth fluorides consisting of a substitutional Pb$^+$ ion next to a F$^-$ vacancy have shown IR emissions (SrF$_2$ at 1.17 eV) when excited in their A_1 absorption bands (SrF$_2$ at 1.87 eV). In contrast to the analogous Pb$^+$(1) centres in KMgF$_3$ they could not be brought to lase. It is shown that this failure occurs because of a loss mechanism in which excited-state absorption leads to an 'upconversion' emission peaking at 2.375 eV for CaF$_2$, 2.361 eV for SrF$_2$ and 2.370 eV for BaF$_2$. Its intensity depends quadratically on the pump power and it can also be excited in the A_3 band in the UV. A theoretical calculation shows that the upconversion emission originates from the relaxed excited state of a F$_A$-centre model rather than from a 6s^{2}7s excited Pb$^+$(1) state and explains its observed temperature dependence. The upconversion is observed in the alkaline-earth fluorides because of an accidental energy resonance $2A_1 = A_3$ that does not occur in KMgF$_3$.

1. Introduction

Tl^0(1) centres in alkali halides (Mollenauer *et al* 1982, 1983) as well as the isoelectronic Pb$^+$(1) centres in KMgF$_3$ (Hörsch and Paus 1987) were shown to be laser active in the near infrared and to have rather attractive properties for tunable lasers. The laser active centres consist of a Tl^0 atom or a Pb$^+$ ion next to an anion vacancy. The electronic configuration is Xe 4f^{14}5d^{10}6s^{2}6p^1 with the ground and first-excited terms of the single p electron, ^{2}P$_{1/2}$ and ^{2}P$_{3/2}$, separated by a large spin–orbit interaction. The strong odd crystal field of the vacancy further splits and shifts the 6p manifold and partly allows electric dipole transitions within the 6p multiplet through admixture of even-parity states. The interplay between the spin–orbit interaction and the crystal field is the reason for the favourable laser properties (Ahlers *et al* 1984, Fockele *et al* 1985, 1989b). Unfortunately, the stability of the Tl^0(1) centres is not very high, which is a disadvantage for the use of this laser. Pb$^+$(1) centres are much more stable. However, the low crystal quality of KMgF$_3$, largely due to the incorporation of oxygen containing scattering centres during crystal growth, has so far prevented commercial use of the Pb$^+$(1)-centre system. An attempt was therefore made to produce laser-active Pb$^+$(1) centres in the alkaline-earth fluorides CaF$_2$, SrF$_2$ and BaF$_2$, where the crystal quality is a great deal better than in KMgF$_3$. These centres could be produced successfully in all three hosts

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and they showed strong emission bands peaking between 1.31 eV (CaF_2) and 1.06 eV (BaF_2) upon excitation at about 1.9 eV at room temperature. A detailed investigation of their optical, magneto-optical and magnetic resonance properties showed that these centres were the isoelectronic analogues of the laser-active $Tl^0(1)$ centres in alkali halides. A calculation of the optical gain factor gave the same values as those for $Pb^+(1)$ centres in $KMgF_3$ and slightly smaller ones than those of $Tl^0(1)$ centres in alkali halides. The centres were found to be stable at room temperature and under illumination by intense light (Fockele *et al* 1989a, Bartram *et al* 1989). In view of this, it was disappointing that none of the $Pb^+(1)$ centres in the three alkaline earth fluorides could be brought to lase, either at room temperature or at 77 K (Huber 1989, Paus 1989). Beyond a certain level, IR emission of these crystals diminished with increasing excitation intensity. It remained an open question as to the kind of competitive de-excitation channel that was operating at high excitation levels and which apparently prevented laser action.

In this paper we report on the discovery of upconversion by excited state absorption of $Pb^+(1)$ centres in SrF_2, CaF_2 and BaF_2. The upconversion emission is the result of an excited-state absorption process and explains the failure to observe the IR laser action. We discuss how this loss mechanism can possibly be avoided on the one hand, while it may be used on the other hand to produce an upconversion laser.

2. Experimental details

The alkaline-earth fluoride crystals were grown from Merck suprapur materials by the Bridgman technique and doped with 0.5 mol.% of PbF_2. The crystals were irradiated with x-rays (50 kV, 30 mA) at 300 K. The best conditions for the formation of only $Pb^+(1)$ centres and for the avoidance of simultaneous production of $Pb^0(2)$ centres are described in Fockele *et al* (1989a).

The optical measurements were performed with a computer-controlled optical spectrometer. The emissions were excited with a dye laser (dye DCM) which was pumped with a 7.5 W argon ion laser. The output of the dye laser at 1.88 eV was about 1 W, of which only approximately 100 mW were incident on the sample due to losses in the optical system (mirrors, lenses, windows etc). The monochromator used was a Spex Doublemate with gratings blazed at 1000 nm, 500 nm and 300 nm. A Northcoast Ge detector EO-817, cooled with liquid nitrogen, was used in the IR and an RCA photomultiplier (cooled to $-40\,°C$), in the visible and UV spectral region. The exciting light intensity could be attenuated in a controllable way. The sample temperature could be varied between 5 K and room temperature.

3. Experimental results

Figure 1 shows the emission bands obtained at 80 K when the $Pb^+(1)$ centres were excited in the so-called A_1 bands peaking between 1.74 and 1.95 eV. The IR emission bands peaking between 1.06 and 1.31 eV were reported previously (see table 1) (Fockele *et al* 1989a). The emission bands at about 2.4 eV, which are at higher energy than the excitation energy of the A_1 band, are reported here for the first time (see table 1 for their photon energies and halfwidth). The spectral band width of the excitation is indicated (bands with index 1 in figure 1). It must be noted that the relative intensities of the IR emission bands and the high-energy bands are not those of figure 1, since different
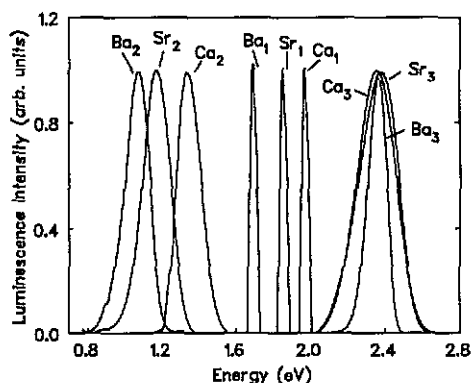
Figure 1. Luminescence bands of Pb$^+$(1) centres in CaF$_2$, SrF$_2$ and BaF$_2$ measured at 80 K when exciting in the A_1 absorption bands. The excitation energy and band width is shown as bands with index 1 (Ca stands for CaF$_2$ etc). The IR luminescence (index 2) is approximately 4×10^4 times more intense than the green upconversion luminescence (index 3) when excited with the maximum power of approximately 100 mW. (This value refers to SrF$_2$.)

Table 1. Energies of the absorption bands A_i^*, their halfwidth, the upconversion emission bands E_3 and halfwidth and the IR emission bands E_e^* of Pb$^+$(1) centres in the alkaline-earth fluorides and KMgF$_3$. All quantities are in eV.

Crystal	A_3^*	A_2^*	A_1^*	$\delta\nu_A^*$	E_e^*	E_3	$\delta\nu_3$
CaF$_2$	4.190	2.728	1.946	0.273	1.308	2.375	0.26
SrF$_2$	3.707	2.653	1.866	0.205	1.172	2.361	0.26
BaF$_2$	3.595	2.523	1.742	0.174	1.057	2.370	0.13
KMgF$_3$	4.35	2.99	1.94	0.244			

* After Fockele *et al* 1989a, b. E_3 is uncertain by ± 0.005 eV. E_3 was measured at 80 K and the other data at 10 K.

detectors and excitation intensities were used. For example, the IR band at about 1.17 eV of SrF$_2$ is approximately 4×10^4 times more intense than that at 2.36 eV for the same (highest) excitation level.

The intensity of the IR emission depends linearly on the intensity of the exciting light in the A_1 band within the range of exciting power available (see figure 2(a) for SrF$_2$). However, the intensity of the emissions at about 2.36 eV ('green' emission) is proportional to the square of the exciting light power (see figure 2(b) for SrF$_2$). This observation clearly shows that the green emission is due to a two-photon process in which the non-relaxed emitting excited state is reached by the addition of twice the energy needed to reach the first excited state of the Pb$^+$(1) centre. Because of the relative weakness of the green emission compared with the IR emission, due to the weak exciting power available, a sublinear behaviour of the IR emission as a result of the competition between itself and the green emission is not seen. The green emission can also be excited in the A_3 band, as shown in figure 3 for CaF$_2$. The same relaxed excited state from which the green emission originates can thus be reached 'directly' by exciting in the A_3 band or 'indirectly' by an upconversion process when exciting in the A_1 band with sufficient light intensity.

The temperature dependences of the IR and green emissions when excited in the A_1 bands are shown in figure 4, parts (a) and (b). At room temperature, the IR emission is only about up to 30% of that at 5 K (figure 4(a)), while the green emission is completely quenched at 200 K (figure 4(b)). The latter is apparently thermally activated in BaF$_2$
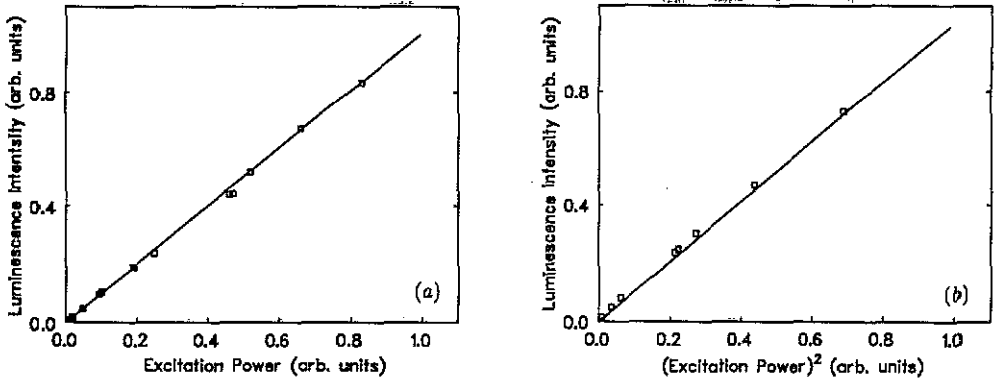
Figure 2. Luminescence intensity measured as a function of the exciting light power for Pb$^+$(1) centres in SrF$_2$. (*a*) IR luminescence at 1.17 eV versus the exciting light power. (*b*) upconversion luminescence at 2.36 eV versus the square of the exciting light power.
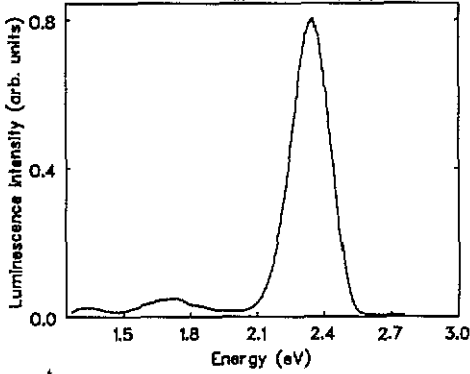

Figure 3. Green luminescence of Pb$^+$(1) centres in CaF$_2$ excited in the A_3 band at 3.4 eV (80 K). The small low-energy emission bands are from impurities in the crystal absorbing also in the UV region.
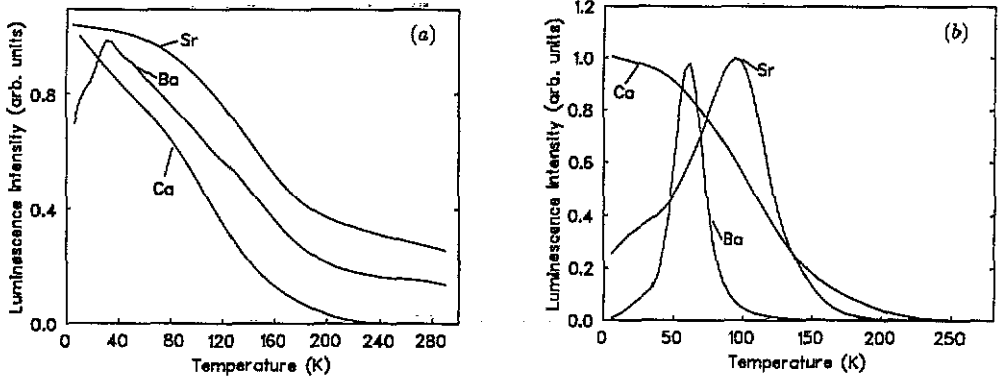

Figure 4. Temperature dependence of the luminescence intensities for Pb$^+$(1) centres in CaF$_2$, SrF$_2$ and BaF$_2$. (Ca stands for CaF$_2$ etc.) (*a*) of the IR luminescence; (*b*) of the green upconversion luminescence.

and SrF_2 with peaks at about 60 and 100 K, respectively, while that of CaF_2 shows no thermal activation. A non-radiative decay channel dominates at higher temperatures.

It should be noted that the IR emissions are also excited in the A_3 bands in the UV and in the A_2 band (see table 1). A similar observation was made for the $Pb^+(1)$ centres in $KMgF_3$ (see table 1). There is, however, one striking difference between alkaline-earth fluorides and $KMgF_3$: *in the alkaline-earth fluorides the photon energy of the transition A_3 is almost exactly twice that of the transition A_1* while this energy resonance is not present in $KMgF_3$. As will be discussed below it is this energy resonance that opens up competitive excitation and de-excitation channels, which are not present in $KMgF_3$ and which prevent the laser action in the alkaline-earth fluorides.

4. Discussion

In the following discussion, specific numerical values are cited for the $Pb^+(1)$ centre in SrF_2. However, the conclusions are generally applicable to all of the alkaline-earth fluorides except where differences are noted explicitly. The $Pb^+(1)$ centres in alkaline-earth fluorides are isoelectronic with $Tl^0(1)$ centres in alkali halides, whose low-lying electronic states have been interpreted successfully in terms of a crystal-field model. The three lowest levels arise from the $6s^2 6p$, ^2P term of the Pb^+ ion under the combined influence of the spin–orbit interaction and an axial crystal field associated with the neighbouring anion vacancy. The energy levels are given as a function of spin–orbit splitting, Δ, and crystal-field parameter, γ, by (Fockele *et al* 1985):

$$W_1 = 0.5\{(\Delta - \gamma) - [(\Delta - \gamma)^2 + 8\gamma^2]^{1/2}\} \tag{1}$$

$$W_2 = 0.5\{(\Delta - \gamma) + [(\Delta - \gamma)^2 + 8\gamma^2]^{1/2}\} \tag{2}$$

$$W_3 = \Delta + \gamma. \tag{3}$$

Optical transitions between these levels, with transition energies $A_1 = W_2 - W_1$ and $A_2 = W_3 - W_1$, are allowed by virtue of the admixture of even-parity states by odd-parity components of the crystal field (Goovaerts *et al* 1981).

A higher excited state observed in excitation spectra was identified by Mollenauer *et al* (1983) as a $6s^2 7s$, $^2S_{1/2}$ state, but the dependence on lattice parameter of the corresponding transition energy, $A_3 = W_4 - W_1$, for $Tl^0(1)$ centres in alkali halides suggested a closer affinity to the Mollwo–Ivey law for the F-band energy (Fockele *et al* 1985). This observation was interpreted as evidence that the final state of the A_3 transition might be characterized alternatively as an excited state of the F_A centre, i.e., an F centre adjacent to a substitutional Tl^+ ion. The A_3 transition energy of the laser-active, perturbed $Pb^+(1)$ centre in $KMgF_3$ also coincides with the F-band energy in that compound (Fockele *et al* 1989b), while the energy of the A_3 band in the excitation spectrum of the $Pb^+(1)$ centre in SrF_2 exceeds that of the F band at 0.85 eV (Fockele *et al* 1989a).

These observations can be explained by comparing the relative stabilities of the $Tl^0(1)$ and F_A centres in KCl and the $Pb^+(1)$ and F_A centres in SrF_2 in their respective ground states. The energy required to transfer an electron from the metal atom or ion to the anion vacancy can be determined by means of a cycle analogous to that employed in the charge transfer model of excitons (Hilsch and Pohl 1930, Born 1933): the metal

atom or ion is removed from the cation site, ionized and restored, and the electron is subsequently placed in the vacancy. The net gain in energy, δE, is given by

$$\delta E = W_1 - I + (\alpha_+ - r_0/r_1)e^2/r_0 + \delta E_g \qquad (4)$$

where W_1 is the negative of the crystal-field stabilization energy given by equation (1), I is the appropriate ionization potential, α_+ is the Madelung constant appropriate to the cation site, r_0 is the nearest-neighbour distance in the perfect crystal, r_1 is the metal–vacancy separation in the relaxed ground state, and δE_g is the binding energy of the F-centre ground state.

The values of the parameters appropriate to the ground state of the $Tl^0(1)$ centre in KCl are: $\Delta = 0.806$ eV, $\gamma_0 = 0.403$ eV, $I = 6.11$ eV (the first ionization potential of Tl), $\alpha_+ = 1.746$, $r_0 = 3.145$ Å, and $\delta E_g = 5.94$ eV. For consistency, rigid-lattice point-ion values are employed for F-centre binding energies (Bartram *et al* 1968). With the assumption that $r_1 = r_0$, these parameter values yield a net gain of $\delta E = 2.84$ eV; thus the F_A-centre configuration is predicted to be more stable than the $Tl^0(1)$ centre configuration in the unrelaxed ground state.

The Madelung constants for alkaline-earth fluorides, defined as the energy of a single positive electronic charge in units of e^2/r_0, are $\alpha_+ = 3.315$ at the cation site and $\alpha_- = -1.762$ at the anion site (Franklin 1968). For the ground state of the $Pb^+(1)$ centre in SrF_2, the remaining parameters have the values $\Delta = 1.15$ eV, $\gamma_0 = 0.64$ eV, $I = 15.03$ eV (the second ionization potential of Pb), $r_0 = 2.50$ Å, and $\delta E_g = 6.95$ eV, yielding a net gain of $\delta E = 4.56$ eV for $r_1 = r_0$. The larger ionization potential in this case is more than offset by the larger Madelung energy, and the F_A centre is again the more stable configuration in the unrelaxed ground state.

The preceeding calculations fail to take account of lattice relaxation. It is found experimentally that a prominent aspect of this relaxation is a displacement of the metal ion towards the vacancy in the ground state ($r_1 < r_0$). The effect of this displacement is to stabilize the $Tl^0(1)$ and $Pb^+(1)$ configurations; except for the additional repulsive energy which is common to both configurations, the F_A-centre configuration is unaffected by the displacement, since there is no electric field at the cation site when the remaining point charges are distributed as in the perfect crystal. ESR spectra suggest a substantial admixture of the two configurations (Goovaerts *et al* 1981, Ahlers *et al* 1986, Fockele *et al* 1985, 1989a, b); i.e., one electron is shared between the metal ion and the vacancy, forming a one-electron bond. A near degeneracy of the two configurations is a condition for the formation of such a bond. The degeneracy condition $\delta E = 0$ in equation (4) is satisfied by $r_0/r_1 = 1.62$ for the $Tl^0(1)$ centre in KCl and by $r_0/r_1 = 1.79$ for the $Pb^+(1)$ centre in SrF_2. The ground-state energy is determined primarily by that of the F centre, but is depressed somewhat by the excessive binding energy associated with delocalization of the electron; the increment of electronic energy gained by delocalization presumably more than offsets the additional repulsive energy involved in the displacement. The excitation energy, A_3, is expected to exceed that of the F centre by the same increment of electronic energy, on the assumption that the W_4 level corresponds to an excited state of the F_A centre. This energy increment appears to be greater for the $Pb^+(1)$ centres in alkaline-earth fluorides than for the $Tl^0(1)$ centres in alkali halides.

These calculated values of r_0/r_1 undoubtedly exaggerate the displacements of the metal ions. Additional relaxation and polarization of the surrounding lattice, which reduces the effective ionic charges and, especially, diminishes the F-centre binding
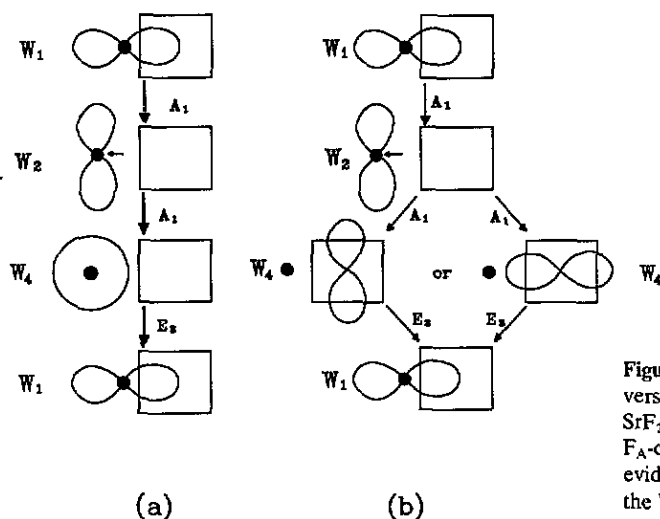
Figure 5. Schematic diagram of the upconversion process in the $Pb^+(1)$ centre in SrF_2. (*a*) $6s^27s$ model of the W_4 state. (*b*) F_A-centre model of the W_4 state. It is not evident from the available data whether the W_4 state is a σ state or a π state.

energy, permits the degeneracy condition $\delta E = 0$ to be satisfied by more modest displacements. More realistic estimates can be obtained with the assumption that the metal ion returns to its perfect lattice position in the relaxed first excited state (W_2) as an expected consequence of bond breaking. Since the quadratic component of the crystal field varies inversely as r_1^3 in the limit of a compact 6p orbital, the ratio of the metal ion–vacancy distance in the relaxed first excited state, r_0, to that in the relaxed ground state, r_1, is given approximately by

$$r_0/r_1 = (\gamma_0/\gamma_1)^{1/3}. \tag{5}$$

The experimental values of γ_1 and the values of r_0/r_1 calculated from equation (5), are, respectively, $\gamma_1 = 0.201$ eV and $r_0/r_1 = 1.26$ for the $Tl^0(1)$ centre in KCl, and $\gamma_1 = 0.280$ eV and $r_0/r_1 = 1.32$ for the $Pb^+(1)$ centre in SrF_2. These values are in much closer accord with inferences from measured superhyperfine interactions (Ahlers *et al* 1986, Fockele *et al* 1989a).

The upconversion process is illustrated schematically in figure 5 both for the $6s^27s$ model and for the F_A-centre model of the W_4 level. Both the excited-state absorption and the visible emission steps in the upconversion process are electric-dipole allowed as charge-transfer transitions in the excited F_A-centre model. They are also allowed by atomic selection rules in the $6s^27s$ model. However, it appears less likely that this state, which lies 7.4 eV above the ground state in the free ion (Moore 1958), is relevant to the A_3 band at 3.707eV.

A hypothetical configuration-coordinate diagram based on the simplifying assumption of linear coupling to a single configuration coordinate, drawn to scale in figure 6, illustrates several features of the upconversion process for the $Pb^+(1)$ centre in SrF_2. The initial step in this process is the absorption of a red photon of energy $A_1 = 1.88$ eV. A pronounced relaxation of the W_2 state, associated with displacement of the Pb^+ ion away from the vacancy, is responsible for the Stokes shift of the IR emission, $E_1 = 1.172$ eV. A second photon of energy A_1 absorbed in the relaxed excited W_2 state induces a transition to the W_4 state. There is an obvious mismatch between the photon energy and the minimum excitation energy in this step, which exceeds the absorption linewidth
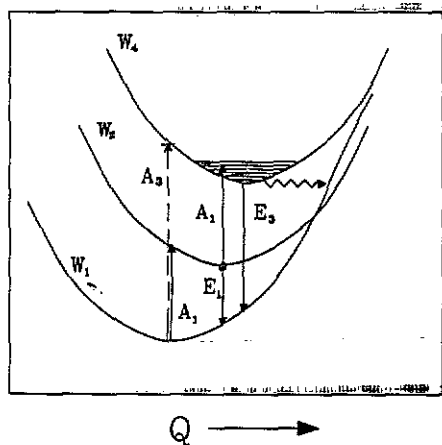
Figure 6. Configuration coordinate diagram illustrating the upconversion process. The W_3 adiabatic potential energy curve is omitted for clarity.

at 10 K. This linewidth increases with temperature, thus enhancing the probability of excited-state absorption. A slight further relaxation of the W_4 state accounts for the remainder of the Stokes shift of the green emission at $E_3 = 2.361$ eV. At still higher temperatures, the green emission is quenched by a competing non-radiative transition either directly to the ground state or to the lower excited states. (The adiabatic potential energy curve for the W_3 state is omitted from the diagram for the sake of clarity.) Thus the temperature dependence of the E_3 emission of the Pb$^+$(1) centre in SrF$_2$ shown in figure 4 is fully explained by this model.

The single-configuration-coordinate, linear-coupling model cannot be strictly correct, since it is not entirely consistent with (1)–(3). However, it has the virtue that all of its relevant parameters can be inferred from optical spectra. In this model, the mismatch, ε, between the photon energy, A_1, and the threshold energy for excited-state absorption is given by

$$\varepsilon = A_1 - 0.5\{(A_3 + E_3 - A_1 - E_1) + [(A_1 - E_1)^{1/2} - (A_3 - E_3)^{1/2}]^2\} \tag{6}$$

and the linewidth for excited-state absorption, $\delta\nu_{ESA}$, which is proportional to the square root of the Huang–Rhys factor, is given in terms of that for ground-state absorption, $\delta\nu_A$, by

$$\delta\nu_{ESA} = \{[(A_3 - E_3)/(A_1 - E_1)]^{1/2} - 1\}\delta\nu_A. \tag{7}$$

The energy mismatch, ε, is compared with the excited-state absorption linewidth, $\delta\nu_{ESA}$, for all three compounds in table 2. It is evident that the mismatch is less than the linewidth in CaF$_2$, but substantially exceeds it in SrF$_2$ and BaF$_2$; consequently, the maximum intensity of the visible emission is expected to occur at $T = 0$ K in CaF$_2$ but at finite temperatures in SrF$_2$ and BaF$_2$, in accordance with figure 4(b).

It is evident from the preceding discussion that satisfaction of the resonance condition $A_3 = 2A_1$, which enables upconversion, is an accidental feature of the alkaline-earth fluorides. Thus, in principle, one can strive either to avoid the resonance condition in order to produce an efficient IR laser, or to satisfy it in order to devise a red-pumped green laser which operates by upconversion.

The former objective, producing an IR laser based on the Pb$^+$(1) centre, involves either changing the host lattice or modifying it by incorporating lattice defects which

Table 2. Comparison of energy mismatch, ε, and linewidth, $\delta\nu_{\text{ESA}}$, in excited-state absorption, calculated from (6) and (7), respectively. The transition energies A_1, A_3 and E_1 and the absorption linewidth, $\delta\nu_{\text{A}}$, are from Fockele *et al* 1989a. The transition energy E_3 is from the present investigation. All quantities listed are in eV.

	CaF_2	SrF_2	BaF_2
A_1	1.946	1.866	1.742
A_3	4.190	3.707	3.595
E_1	1.308	1.172	1.057
E_3	2.38	2.36	2.37
$\delta\nu_{\text{A}}$	0.273	0.205	0.174
ε	0.145	0.291	0.124
$\delta\nu_{\text{ESA}}$	0.189	0.078	0.060

perturb the crystal field. Both of these aspects are exemplified by the laser-active $Pb^+(1)$ centre in $KMgF_3$.

The latter objective, devising an upconversion laser, may be accomplished by exploiting the quadratic dependence of the green emission on pump power; high pump intensity populates the W_4 level at the expense of the W_2 level. The population of the W_4 level is ultimately limited by saturation effects and by non-radiative deexcitation. However, the strong electron–lattice coupling ensures that the final state is effectively unpopulated, thus facilitating inversion; i.e., the upconversion laser would be a vibronic laser. It also provides a broad pump band in the red and a wide tuning range in the green. It is clear from the temperature dependence of the green emission intensity that the upconversion laser would operate most efficiently at liquid nitrogen temperature, and that it would not operate at all at room temperature. Nevertheless, such a device, which could be pumped by a semiconductor laser, could prove to be a useful laboratory tool.

In summary, the observation of upconversion in the $Pb^+(1)$ centre in alkaline-earth fluorides serves not only to explain the failure of this system to operate successfully as an IR laser, but also suggests its exploitation in a red-pumped, tunable green laser.

Acknowledgment

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