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f-f and f-d transition interference in Sm^{2+}:SrFCl

R. Jaaniso* and H. Bill
Groupe de Physico-Chimie du Solide, Université de Genève, 30 quai Ernest Ansermet, 1211 Genève 4, Switzerland
(Received 6 March 1991)

The $^5D_3(4f^6)$-$^7F_0(4f^6)$ transition of Sm^{2+} in SrFCl is found to be anomalously strong and it exhibits an asymmetric line shape, which is interpreted in terms of resonant interaction between the $^5D_3$ excited state and the vibronic levels of a low-lying $4f^5 5d$ electronic state. The electronic coupling strength is estimated to be on the order of 100 cm^{-1}. The symmetry species of interacting levels are identified, and the possibility of an $E \times (b_1 + b_2)$ type of Jahn-Teller effect in the $4f^5 5d$ state is discussed.

I. INTRODUCTION

An interference of transition matrix elements can occur for transitions with a common initial (final) state and coupled final (initial) states. A case of special interest is with (quasi-) resonant coupling between a discrete state and a continuum of states, which produces asymmetric lines or antiresonances in the spectrum. This effect was analyzed by Fano, with application to the spectra of autoionizing states in rare gases.[1] Later the interference of sharp transitions with the (free- or conduction-) electron continuum has been found and studied, both experimentally and theoretically, in the spectra of molecules[2] and solids.[3]

In impurity solids, under the condition of a huge number of (energetically quasicontinuous) vibrational degrees of freedom, the zero-phonon lines, overlapping with the vibronic spectrum of another electronic transition, also show characteristic interference profiles.[4,5] Although in this case the continuum has a different physical origin, the Fano line-shape formula is shown to be formally applicable under reasonable approximations.[4]

We report evidence about the crystal-field-induced configuration mixing in Sm^{2+}:SrFCl, which results in the $^5D_3(4f^6)$-$^7F_0(4f^6)$ purely-electronic-line(s) (PEL) interference with the vibronic band of a $4f^6$-$4f^5 5d$ interconfigurational transition. The host crystal, SrFCl, has point group D_{4h},[6] and the Sm^{2+} ions enter substitutionally at cationic Sr^{2+} sites with C_{4v} symmetry. The lack of inversion symmetry at the static crystal sites is of central importance for the effect observed. There are some examples,[7,8] where the strong dynamic mixing of closely spaced $4f^6$ and $4f^5 5d$ states of opposite parity is considered to explain the vibronic structure superimposed on the f-d bands. In the situation of a cubic crystal site[8] the mixing can occur only in a dynamic way (by odd vibrations) and the PEL will not be influenced. It is the odd part of the crystal field, which enables the interference of parity-forbidden f-f PEL with strong electric dipole f-d transi-

tions.

As compared to the earlier observations of Fano lines in the vibronic spectra (detected on the strong background absorption as relatively small antiresonances),[4,5] the above-mentioned transitions of Sm^{2+}:SrFCl show a strong and very clear effect, with the absorption falling nearly to zero value at the point of maximum destructive interference.

II. EXPERIMENTAL

The single crystals with samarium concentration of 0.3% (atomic weight units) were grown by the Czochralski method in an ultrapure argon gas atmosphere. Absorption spectra were recorded on a Cary model 2300 spectrophotometer. The samples mounted in a liquid-helium cryostat (Oxford Instruments, $C2$) were oriented with the crystallographic (C_4) axis parallel to the direction of the light beam (i.e., the α spectra were recorded).

III. RESULTS AND DISCUSSION

In Fig. 1 the absorption spectra in the region of the first strong band due to the allowed f-d transitions are presented. The weak and sharp line visible at the right-hand edge of Fig. 1 can be attributed to the $^5D_2(E)$-$^7F_0(A_1)$ transition within $4f^6$ configuration. At longer wavelengths (up to 700 nm, not shown in Fig. 1) only the $^5D_1(E)$-$^7F_0(A_1)$ line has been found at $T = 4.2$ K. Wavelengths for corresponding fluorescence lines (determined at 5 K)[9] coincide with our values (563.55 nm and 632.43 nm, respectively, $T = 4.2$ K) within the calibration error (± 1 cm^{-1}). The symmetry assignments for the excited states are given above following the selection rules of C_{4v} point group, which permit only the E-A_1 type transitions from the A_1 ground state in an α-polarized spectrum.

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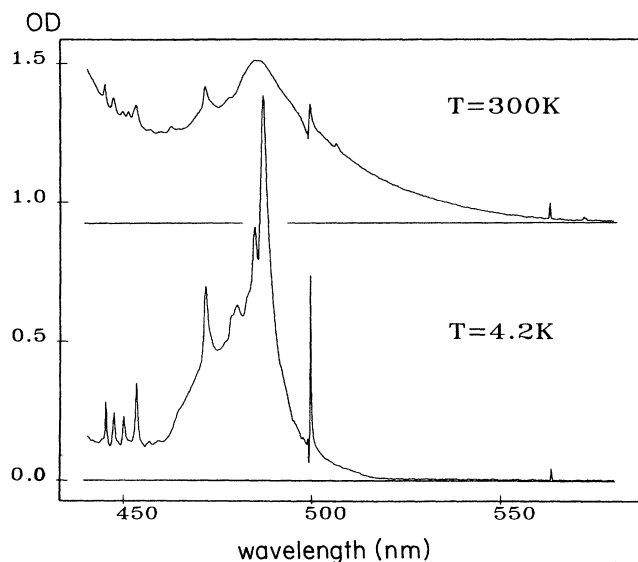

FIG. 1. Absorption spectra of Sm^{2+}:SrFCl in the region of the lowest $4f^6$-$4f^5 5d$ band, recorded in α polarization at $T=4.2$ K, and at room temperature. Sample thickness 1.3 mm, spectral resolution 0.2 nm. O.D. stands for optical density.

Several sharp features are also present in the vicinity of the broad f-d band. Part of this structure remains clearly visible in the room-temperature spectrum, which indicates its f-f origin. In the following, we will focus on the sharp resonance, located at ≈ 500 nm and enlarged in Fig. 2. It would be derived from the $^5D_3$ (excited) state, as verified by comparison of the $^5D_{1,2,3}$-$^7F_0$ transitions energies of the Sm^{2+} and isoelectronic Eu^{3+} ions, respectively (reduction of the Eu^{3+} transitions energies by 20% gives approximately the corresponding values for Sm^{2+}).[10]

The $^5D_3$ multiplet splits into five Stark components
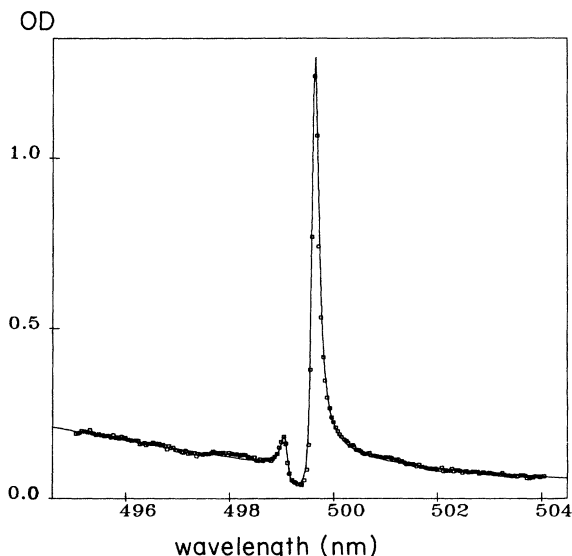
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FIG. 2. Absorption resonances of Sm^{2+} ion in SrFCl originating from two $^5D_3(E)$-$^7F_0(A_1)$ transitions. $T=4.2$ K.

transforming as A_2, B_1, B_2, and $2E$. Obviously, these levels are allowed to interact with $4f^5 5d$ states having the same symmetry. In case of strong interference effect, however, only the $5d$ levels terminating the electric dipole transitions from the ground state should be considered. At low temperatures (no thermal vibrations in the ground state) these can be E (α and σ polarization) or A_1-type (π polarization) vibronic levels. Comparison of the possible state symmetries shows now that only the E-type levels can be responsible for the $^5D_3$-$^7F_0$ PEL interference with the f-d band.[11] The presence of two E components in $^5D_3$ multiplet is in accordance with the double peak structure of the spectrum shown in Fig. 2.

The integral intensity of the f-d band, shown in Fig. 1, is practically independent of temperature, which suggests the Franck-Condon character of the corresponding electronic transition. This means that the $5d$ electronic state should also transform according to the E representation, as the selection rules forbid the transitions to all other types of states in α polarization. Further identification of the actual $5d$ state needs a more detailed analysis. Although this is thoroughly performed for Sm^{2+} in CaF_2-type crystals,[12] the different character of the d-electron crystal field splitting in SrFCl makes such an analysis a matter of special investigation.[13]

We will proceed with the quantitative description of the $^5D_3$-$^7F_0$ resonances. In general, the vibronic continuum, characterized by a high-dimensional coordinate space, has to be considered in each electronic state involved. As a result, quite complex vibronic coupling and the initial-state averaging problem have to be resolved. However, one can successfully separate the subproblem of zero-phonon-line interference with the vibronic part of another electronic transition, and obtain, at $T=0$ K, a line-shape formula similar to that in atomic cases.[4] The essential approximations which lead to this result can be summarized as follows: (i) The adiabatic approximation is valid for the zeroth order wave functions (defined for the system without discrete-continuum interaction); (ii) the matrix elements of these wave functions can be calculated in the Condon approximation; (iii) radiative and phonon-assisted relaxation processes can be neglected. On the other hand, the presence of only one single zero-phonon transition is not a limitation, in principle, for the analogy with the atomic case. Therefore, to describe the spectrum depicted on Fig. 2, Fano's result for many excited discrete states[1] should be usable, provided the above listed conditions (i)-(iii) are fulfilled. After some algebra, the absorption profile $K(v)$ in the presence of two discrete states may be written as[14]

$$\frac{K(v)}{K_0(v)} = (1-p) + p\frac{(\xi_1\xi_2 + \xi_1 q_2 + \xi_2 q_1)^2}{(\xi_1\xi_2)^2 + (\xi_1 + \xi_2)^2}, \quad (1)$$

where

$$\xi_1 = \frac{v - v_1}{(\Gamma_1/2)}, \quad \xi_2 = \frac{v - v_2}{(\Gamma_2/2)},$$

and $K_0(v)$ is the absorption profile because of the continuum alone. The parameters (v_i, Γ_i, q_i) correspond to two discrete levels ($i=1,2$) and describe the resonant frequency, linewidth, and asymmetry, respectively. The parameter p accounts for the additional background absorption if

several continua are present ($0 < p \le 1$, where the equality holds for the single continuum).

The most sensitive point with respect to justifiability of conditions (i) and (ii) is the degeneracy of the excited $5d(E)$ electronic state. We first notice that the actual *f-d* transition is strongly coupled to the phonons, as there is no PEL in the spectrum, which could be associated with this transition. At the same time, the *f-d* band has a non-Gaussian shape at room temperature, and, at $T = 4.2$ K, the structure (consisting of two peaks separated by 100 cm^{-1}) appears in the center of the band. In the case of large Stokes losses, the latter features cannot be understood when interpreted as resulting from transitions to nondegenerate electronic states, but, instead, are both characteristic for the transition to an E-type electronic state subject to the Jahn-Teller effect.[15] Both symmetry-allowed Jahn-Teller active modes (b_1 and b_2) should be involved, as the purely static $E \times b_1$ as well as $E \times b_2$-type effects are known to result in a spectral profile comparable to the one in the case of a nondegenerate final state.[16]

The structure in the center of the $A_1 \rightarrow E$ transition spectrum should correspond to the excited vibronic levels at (or above) the central maximum of the lower adiabatic sheet.[15] The vibronic levels coupled with the purely electronic $^5D_3$ states lie ≈ 500 cm^{-1} lower, and, therefore, can quite reasonably be considered as located in two different Jahn-Teller conformations. That is to say, one can effectively define two electronic wave functions ($|x\rangle$ and $|y\rangle$) for these conformations and describe the interference pattern still in the frame of the adiabatic approximation. Then, the problem should be analyzed in C_{2v} symmetry. It is easy to verify that the transitions to the electronic states $|x\rangle$ and $|y\rangle$ are of the Franck-Condon type (i.e., allowed in static lattice) and the static interaction between these states and $^5D_3$ ($E \rightarrow B_1 + B_2$) states is also "permitted" by symmetry. Consequently, the Jahn-Teller effect can be considered in the analysis of interfering transitions as a static one and our previous discussion will not be seriously altered. The new feature is that, instead of one continuum, two vibronic continua with quite symmetric properties are expected.

To fit the experimental spectrum, the spectral resolution of the monochromator (3 cm^{-1} in case of spectrum shown in Fig. 2) has to be taken into account. For that, the function (1) was convoluted with an apparatus function of triangular form. The best fit result, achieved at the values of the parameters $v_1 = 20037.0$ cm^{-1}, $v_2 = 20014.5$ cm^{-1}, $\Gamma_1 = 4.6$ cm^{-1}, $\Gamma_2 = 4.8$ cm^{-1}, $q_1 = 1.4$, $q_2 = -4.6$, $p = 0.65$, is shown as a solid line in Fig. 2. The fitting errors were estimated to be ± 0.2 cm^{-1} for v_1 and v_2, and $\pm$ (3–5)% for other parameters.[17]

To give an exact physical definition of the listed parameters, i.e., to relate them to the interaction matrix elements on zeroth-order wave functions, one has to perform the diagonalization procedure in full form along the lines sketched by Fano.[1] This treatment is now under progress for the model representing Sm^{2+} in SrFCl. It is, however, clear from previous treatments[1,14] that the linewidths (Γ_1, Γ_2) do measure the coupling strength between the discrete state and the continuum states. Under conditions

(i) and (ii), as it is precisely shown for a single zero-phonon transition,[4] the electronic and vibrational parts of the interaction matrix elements factorize as

$$\Gamma = 2\pi |\Lambda|^2 G_2(v),   (2)$$

where $\Lambda = \langle f | V_u | d \rangle$ is the electronic matrix element of interaction operator V_u, and $G_2(v)$ is the vibrational overlap factor at resonance frequency. Assuming the set of normal coordinates in the $4f^6$ excited and ground state to be the same, the value of $G_2(v)$ may be calculated from the normalized *f-d* band shape. (Although this statement is not exactly valid in the presence of the Jahn-Teller effect, it can be used, at least in the case of allowed *f-d* transition, to obtain a rough estimate.) Normalizing the *f-d* band (lower spectrum in Fig. 1, $T = 4.2$ K) in the spectral interval of 455–520 nm one obtains $G_2 = 6 \times 10^{-5}$ cm at $v = 20030$ cm^{-1}. Insertion of this value together with average linewidth $\Gamma = (\Gamma_1 + \Gamma_2)/2$ into the expression (2) leads to $|\Lambda| = 110$ cm^{-1}, which is at least one order smaller than the main electronic interactions in free ions[10] or in the d-electron crystal-field effects (in cubic crystals).[12]

The parameter p, with a value less than one, can be related to the presence of two vibronic continua arising from electronic states $|x\rangle$ and $|y\rangle$. This effect is strictly analogous to the case of several orthogonal continua in autoionization phenomenon.[1] In the vibronic problem, in addition, the p value may be effectively lowered by the small deviations from conditions (i) and (ii). The same statement is valid for condition (iii), which can now be formulated more explicitly: it requires the phonon relaxation times to be much longer than the inverse values of linewidths [for the average linewidth $(2\pi c \Gamma)^{-1} = 10^{-12}$ s at $T = 4.2$ K].

IV. CONCLUSION

We have shown that the anomalous spectral features (asymmetric line shape, strong intensity) of $^5D_3$-$^7F_0$ transition of Sm^{2+} ion in SrFCl are due to the mixing of $^5D_3(2E)$ and $4f^5 5d(E)$ states with the estimated electronic coupling strength of the order of 100 cm^{-1}. The shape of the actual *f-d* transition spectrum can be accounted for by the $E \times (b_1 + b_2)$-type Jahn-Teller effect in the $4f^5 5d(E)$ state. Further investigation would be exciting from this side of the problem, as the presence of resonant *f-d* mixing leads, in fact, to the coherent motion between two Jahn-Teller conformations at the energies of $^5D_3$ levels.

The remarkable point, to be explained, is also the difference compared to the case of BaFCl host, where the interference effect of Sm^{2+} $^5D_3$-$^7F_0$ lines seems to be absent[18] in spite of the same crystal structure and a very similar *f-d* absorption.

ACKNOWLEDGMENTS

R. JAANISO AND H. BILL

*Permanent address: Institute of Physics, Estonian Academy of Sciences, Tartu 202400, Estonia, U.S.S.R.

[1]U. Fano, Phys. Rev. **124**, 1866 (1961).

[2]See, for example, A. L. Sobolewski and W. Domcke, J. Chem. Phys. **86**, 176 (1987), and references therein.

[3]See, for example, A. Shibatani and Y. Toyozawa, J. Phys. Soc. Jpn. **25**, 335 (1968), and references therein.

[4]M. D. Sturge, H. J. Guggenheim, and M. H. L. Pryce, Phys. Rev. B **2**, 2459 (1970).

[5]M. J. Taylor, Phys. Rev. Lett. **23**, 405 (1969); V. A. Arkhangel'skaya and P. P. Feofilov, Opt. Spectrosc. (USSR) **28**, 657 (1970); M. S. Skolnick et al., J. Phys. C **15**, 3333 (1982).

[6]For crystal structural parameters, see M. Sauvage, Acta Crystallogr. Sec. B **30**, 2786 (1974).

[7]W. E. Bron and M. Wagner, Phys. Rev. **145**, 689 (1966).

[8]T. Tsuboi (unpublished).

[9]G. Grenet et al., Phys. Rev. B **22**, 5052 (1980).

[10]G. H. Dieke, Spectra and Energy Levels of Rare Earth Ions in Crystals (Wiley, New York, 1968).

[11]This conclusion remains valid at $T \neq 0$ if the f-d electronic transition is of Franck-Condon type.

[12]A. Yanase, J. Phys. Soc. Jpn. **42**, 1680 (1977).

[13]The difference between the general structure of the divalent rare-earth ions f-d spectra in fluorite and MFX-type crystals has been pointed out earlier; see D. S. McClure and Z. Kiss, J. Chem. Phys. **39**, 3251 (1963).

[14]See also W. Leonski, R. Tanas, and S. Kielich, J. Opt. Soc. Am. B **4**, 72 (1987).

[15]Yu. E. Perlin, L. S. Kharchenko, and M. Frackowiak, Zh. Eksp. Teor. Fiz. **88**, 642 (1985) [Sov. Phys. JETP **61**, 377 (1985)].

[16]J. H. Hougen, J. Mol. Spectrosc. **13**, 149 (1964).

[17]The use of a Gaussian apparatus function gave the result within these errors, except for a slight ($\approx 10\%$) increase in the value of parameter p.

[18]See spectra in Z. J. Kiss and H. A. Weakliem, Phys. Rev. Lett. **15**, 457 (1965); A. S. M. Mahbub'ul Alam and B. Di Bartolo, J. Chem. Phys. **47**, 3790 (1967); J. C. Gâcon, G. Grenet, J. C. Souillat, and M. Kibler, J. Chem. Phys. **69**, 868 (1978).