Configuration Interaction in Jahn-Teller Systems: Homogeneous Broadening of Zero-Phonon Lines Due to Nonradiative Transitions

M. Montagna, O. Pilla, and G. Viliani
Dipartimento di Fisica, Università di Trento, I-38 050 Povo, Trento, Italy, and Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche, Trento, Italy
(Received 14 April 1980)

Fano's theory of configuration interaction has been extended to Jahn-Teller systems. Homogeneous broadening and shift of the zero-phonon lines are directly connected with interlevel spin-orbit interaction and with the density of states of the interacting continuum. Application to $MgO:V^{2+}$ and $Al_2O_3:Cr^{3+}$ gives excellent agreement between theory and experiment.

PACS numbers: 78.70.-w, 71.55.-i

As is well known, nonradiative transitions (NRT) are of primary importance in determining the optical properties of impurity centers in solids, and in spite of the difficulties inherent in their experimental and theoretical study such processes have recently attracted a lot of work.[1-4]

From the experimental standpoint, difficulties arise from the necessity of evaluating NRT rates indirectly from emission measurements (quantum yield, decay times, etc.), whereas theoretical difficulties consist in general of the poor knowledge of the nonadiabatic operator, of the importance of anharmonic effects,[5] and of the coupling of the impurity to the continuum of vibrational states of the host crystal. A further basic complication is often introduced by electronic degeneracy, which brings into play Jahn-Teller coupling.

This being the situation, one has in general to resort to very simplified models[6-8] involving only one vibrational mode and neglecting the Jahn-Teller effect; such models are largely phenomenological and are useful for determining, for instance, the temperature dependence of NRT, but are of little use for computing the absolute value of the radiationless transition rates.

A few well-known systems ($MgO:V^{2+}$, $MgO:Cr^{3+}$, $Al_2O_3:Cr^{3+}$) exist, however, for which it is possible to develop a nonphenomenological theory which takes into account, at least approximately, the most important effects that have been neglected so far in many cases. In the present Letter we shall show that the widths of the four spin-orbit components of the ${}^4A_2$-${}^4T_2$ zero-phonon transition are determined by fast nonradiative decay from ${}^4T_2$ to the underlying ${}^2T_1$ and ${}^2E$ levels (see Fig. 1), and that such widths can be computed with quite good accuracy employing Fano's theory of configuration interaction.[9,10] In this way it will become clear why in these systems the simple theory of Ham's quenching, which works very well in $KMgF_3:V^{2+}$,[11] if applied in the usual way cannot reproduce the observed splittings.[12,13]

Our starting experimental fact is that the spin-orbit components of the ${}^4A_2$-${}^4T_2$ zero-phonon line in our systems are all mostly homogeneously broadened. This was directly verified in $Al_2O_3:Cr^{3+}$ by negative line-narrowing measurements,[14] while in the case of $MgO:V^{2+}$ the evidence is less direct and is given by the Lorentzian shape of the three components[12,13] (two of the four levels are nearly degenerate), as shown in Fig. 2, which is taken from Ref. 13.

As regards the nature of the operators which cause the NRT, we note that ${}^4T_2$-$({}^2T_1, {}^2E)$ mixing can only be caused by the interlevel spin-orbit

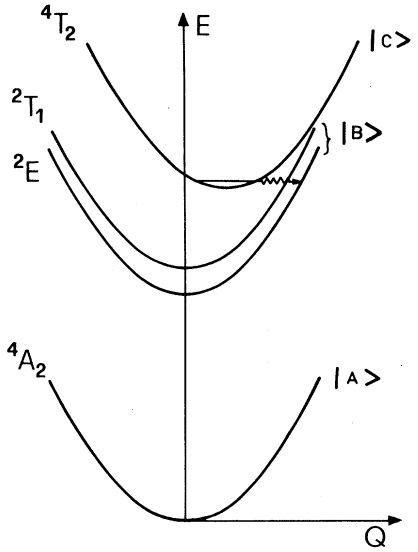

FIG. 1. Schematic energy-level diagram for d^3 ions in cubic symmetry, as a function of a generic normal coordinate.

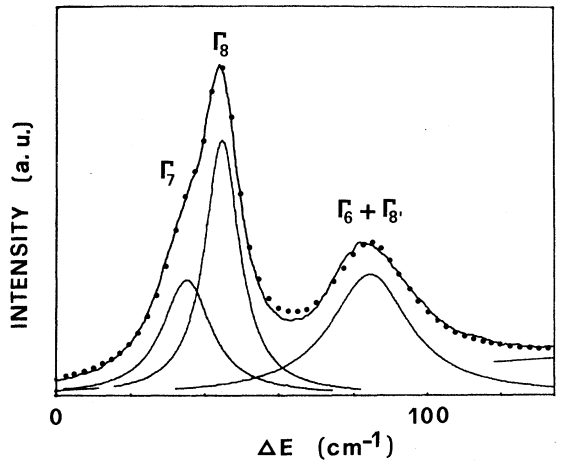

FIG. 2. $^4A_2$-$^4T_2$ zero-phonon line of MgO:V^{2+}. Full line, experimental excitation spectrum at $T = 8$ K; dots, fitting as sum of the three underlying Lorentzian curves. Fitting with Gaussians yields much worse agreement. Labels indicate the relative vibronic states (as in Ref. 13).

interaction, $H_{s.o.}$, which in these systems is quite strong: on the other hand, symmetry arguments require the Jahn-Teller effect on $^4T_2$ to be taken into account in order to explain the width of the low-energy component of $^4T_2$, which transforms according to the Γ_7 irreducible representation (IR) of O_h. In fact, $H_{s.o.}$ only couples states belonging to the same IR, and Γ_7 is not contained in $^2T_1$ and ^2E. Therefore, we need the Jahn-Teller effect to mix the *electronic* part of $\Gamma_7(^4T_2)$ with $\Gamma_6(^4T_2)$ and $\Gamma_8(^4T_2)$. We shall neglect anharmonic effects[5] because the energy gaps between $^4T_2$, $^2T_1$, and ^2E are small, which makes the anharmonic corrections to the rather large vibrational overlaps not very important.

The Hamiltonian will be written in the form $H = H_0 + H_{JT} + H_{s.o.}$, where H_0 contains all of the adiabatic terms, including the first-order spin-orbit interaction within the state $^4T_2$ (henceforth state $|C\rangle$; see Fig. 1), $H_{s.o.}$ is the interlevel spin-orbit interaction, and H_{JT} is the Jahn-Teller Hamiltonian relative to ϵ_g modes which have prominent coupling in our systems. The line shape of the transition from the vibrational ground state of $^4A_2$ to the spin-orbit components of the "zero-phonon" state of $^4T_2$ will be broadened by configuration interaction with $^2T_1$ and ^2E (states $|B\rangle$ in Fig. 1), which is the same as saying by NRT from $|C\rangle$ to $|B\rangle$. By applying Fano's theory[9] to the Jahn-Teller case, and assuming that $|A\rangle \rightarrow |B\rangle$ radiative transitions are forbidden, and since $|B\rangle$ practically have the same equilibrium positions as $|A\rangle$, we find for the line-shape factor of each spin-orbit component, $|\alpha(E)|^2$, a Lorentzian shape, whose width is $\Delta(E) = \Delta_1(E) + \Delta_\epsilon(E)$, and whose peak energy is shifted by an amount $F(E)$ (Lamb shift). These quantitites are given by

$$\Delta_1(E) = (2\pi/\hbar)|\textstyle\sum_R b_{00'}{}^R\langle\varphi^B|H_{s.o.}|\varphi_R{}^C\rangle|^2 G_1(\hbar\Omega_1 = E - E_B{}^0), \tag{1}$$

$$\Delta_\epsilon(E) = (2\pi/\hbar)\textstyle\sum_n \int d\Omega_\epsilon |\sum_R b_{0n'}{}^R(\Omega_\epsilon)\langle\varphi^B|H_{s.o.}|\varphi_R{}^C\rangle|^2 G_1(\hbar\Omega_1 = E - E_B{}^0 - \hbar\Omega_\epsilon), \tag{2}$$

$$F(E) = (1/2\pi)\mathrm{P}\int dE'\,\Delta(E')/(E - E'). \tag{3}$$

In these equations, P means "principal part of"; $G_1(\Omega_1)$ is the contribution of totally symmetrical modes to the multiphonon normalized absorption spectrum, R is the irreducible representation of the electronic state, and $b_{0n'} = \langle 0|n_\epsilon'\rangle$ are overlap integrals between undisplaced and Jahn-Teller-displaced vibrational wave functions. We may note that Eq. (2) can be greatly simplified by assuming that ϵ_g modes have just one frequency, ω_ϵ; this is not expected to be a very serious limitation in that the main role of ϵ_g modes is to mix the electronic states within $^4T_2$, the task of ensuring resonance between the vibronic states $|\psi^C\rangle$ and $|\psi^B\rangle$ being left to α_{1g} modes, whose frequency varies continuously. This assumption means making $b_{0n'}(\Omega_\epsilon) \rightarrow b_{0n'}\delta(\Omega_\epsilon - \omega_\epsilon)$ in (2). The important thing is that the matrix elements of $H_{s.o.}$ are well known; the $b_{0n'}$ coefficients have to be evaluated numerically by diagonalizing $H_0 + H_{JT}$, whereas G_1 can be evaluated by assuming a continuous Pekarian shape for the absorption spectrum once the Huang-Rhys factor S_0 relative to α_{1g} modes is known. The latter may be evaluated by the experimental spectrum and by knowledge of the Jahn-Teller energy.

As regards the application to Al_2O_3:Cr^{3+}, it should be noted that the experimental $^4A_2$-$^4E(^4T_2)$ zero-phonon line shape does not show any structure, indicating that the electronic states are strongly (and roughly equally) mixed in each of the four zero-phonon states of $^4E(^4T_2)$. In such a situation the four zero-phonon lines are expected to be more or less equally broadened and the

width can be computed by using an averaged value of the squared matrix element of $H_{s.o.}$. For the calculation, the value $\zeta = 170$ cm^{-1} has been used for the spin-orbit–coupling constant,[15] whereas to evaluate $G_1(\Omega)$ we used the Pekarian parameters of Ref. 8. Alternatively, $G_1(\Omega)$ can be estimated by the experimental absorption spectrum of Margerie[16]; the two results agree within 10%. The width of 31.6 cm^{-1} we obtain for each of the four lines compares very well with the low-temperature overall experimental value[16] of about 45 cm^{-1}, especially because the hidden spin-orbit splitting of the experimental spectrum makes it look broader. It should be noted that a more precise test is not possible in this case because it is not known how much of the experimental width is due to unresolved spin-orbit splitting and how much to homogeneous broadening of the single components. This is mainly due to the fact that Ham and crystal-field quenchings of the spin-orbit splitting are unknown. On the other hand, the computed order of magnitude of homogeneous broadening must be correct, because otherwise either the structure should be resolved, or the line should be much broader.

The accuracy of the present results should be compared with previous calculations based on simpler or more complicated models.[8,17] The model of Ref. 8 yields a width which is ten times larger than the experimental one, whereas the disagreement is even worse in the case of Ref. 17 since the computed bandwidth is two orders of magnitude smaller than the observed *(homogeneous)* one.

A more stringent test of the theory can be performed on MgO:V^{2+}, because in this case three of the four zero-phonon lines are resolved (see Fig. 2). Taking for the average of the totally symmetrical vibrational energy the value $\hbar\omega_1 = 500$ cm^{-1} which well reproduces the absorption band with a Pekarian curve, $E_{JT} = 150$ cm^{-1}, and $\hbar\omega_\epsilon = 300$ cm^{-1}, we get $S_0 = 1.3$. This determines G_1; the spin-orbit coupling constant is $\zeta = 136$ cm^{-1}.[18] With these parameters we obtain the widths, shifts, and splittings reported in Table I, where for comparison the values computed without including the Jahn-Teller effect are also reported. If we consider that the relative intensities of the components have been accounted for elsewhere,[13,19] we see that the agreement among observed and calculated quantities is excellent, indicating that the proposed mechanism for NRT (i.e., spin-orbit interaction plus Jahn-Teller effect) is basically correct.

It is noteworthy that the splitting as computed in the present paper are in better agreement with experiment than are the ones computed in Refs. 12 and 13 by diagonalizing $H_{JT}+H_{s.o.}$ but by neglecting the spreading of $|B\rangle$ levels. It appears that in the cases where fast nonradiative processes take place which cause appreciable Lamb shift of the levels, the useful and simple theory of Ham quenching cannot correctly reproduce the level energies if second-order spin-orbit interaction with the continuum is not properly taken into account. This explains the remarkable differences existing between the spectra of MgO:V^{2+} and of the similar system KMgF$_3$:V^{2+}. In the latter the $^2T_1$ and ^2E levels lie higher in energy than $^4T_2$, so that fast nonradiative transitions do not take place, the lines are much sharper, and Ham's theory works well.[11,19]

We wish to stress that in our calculation we made use of no independent fitting parameter; in fact, ζ is fixed by crystal field analysis, E_{JT} is deduced by other arguments,[19] and G_1 is determined by the absorption spectrum. The agreement could have been improved by little adjustments of the parameters' values but we avoided doing so on purpose, in order to show the validity

TABLE I. Experimental and calculated widths and splittings for the $^4A_2$-$^4T_2$ zero-phonon line spin-orbit components of MgO:V^{2+}. All data in inverse centimeters.

IR	Widths Expt.	Widths Calc.	Lamb shift	Splittings Expt.	Splittings Calc.[a]	Splittings Calc.[b]
Γ_7	16±3	13.5 (0)[c]	8.2	0	0	0
Γ_8	11±1	10.2 (5.8)[c]	4.0	10	14.4	18.6
Γ_6	26±3	17.3 (27.2)[c]	6.0	50	42.8	45.0
$\Gamma_{8'}$		25.0 (38.3)[c]	20.4		56.0	43.8

[a]With Lamb shift. [b]Without Lamb shift. [c]Without Jahn-Teller effect.

of the present method as compared to previous ones[8,17] which could not even give the correct order of magnitude.

The present theory can be improved by taking into account interaction among discrete levels and in this way it will hopefully be possible to explain the puzzling spectra of other systems. Work on MgO:Cr^{3+} and Cs_2SiF_6:Mn^{4+} is in progress.[20,21]

The authors wish to thank R. Englman, J. Jortner, E. Sigmund, N. Terzi, and M. Wagner for useful discussions.

[1]R. Englman, *Nonradiative Decay of Ions and Molecules in Solids* (North-Holland, Amsterdam, 1979), and references therein.

[2]F. K. Fong, *Theory of Molecular Relaxation* (Wiley, New York, 1975).

[3]A. M. Stoneham, *Theory of Defects in Solids* (Clarendon, Oxford, 1975).

[4]See, for instance, the Proceedings of the NATO School on Radiationless Processes, Erice, 1979, edited by B. Di Bartolo (to be published).

[5]M. D. Sturge, Phys. Rev. B 8, 6 (1973).

[6]R. Englman and R. Barnett, J. Lumin. 3, 37 (1970).

[7]R. Barnett and R. Englman, J. Lumin. 3, 55 (1970).

[8]W. H. Fonger and C. W. Struck, Phys. Rev. B 11, 3251 (1975).

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

[10]U. Fano and J. W. Cooper, Rev. Mod. Phys. 40, 441 (1968).

[11]M. D. Sturge, Phys. Rev. B 1, 1005 (1970).

[12]N. B. Manson and M. D. Sturge, to be published.

[13]G. Viliani, O. Pilla, M. Montagna, and A. Boyrivent, to be published.

[14]A. Monteil and E. Duval, J. Lumin. 18–19, 793 (1979).

[15]S. Sugano and M. Peter, Phys. Rev. 122, 381 (1961).

[16]J. Margerie, C. R. Acad. Sci. 257, 2634 (1962), and thesis, University of Paris (unpublished).

[17]Yu. E. Perlin, B. S. Tsukerblat, and E. I. Perepelitsa, Zh. Eksp. Teor. Fiz. 62, 2265 (1972) [Sov. Phys. JETP 35, 1185 (1973)].

[18]The values of the input parameters were taken from Ref. 14.

[19]M. Montagna, O. Pilla, and G. Viliani, J. Phys. C 12, L699 (1979).

[20]A. Boyrivent, E. Duval, M. Montagna, G. Viliani, and O. Pilla, J. Phys. C 12, L803 (1979).

[21]N. B. Manson, Z. Hasan, and C. D. Flint, J. Phys. C 12, 5483 (1979).

Microwave Enhancement of Superconductivity in Aluminum Tunnel Junctions

James T. Hall, Louis B. Holdeman, and Robert J. Soulen, Jr.
Center for Absolute Physical Quantities, National Bureau of Standards, Washington, D. C. 20234
(Received 28 July 1980)

Microwave radiation (0.1 to 12 GHz) was propagated in a microstrip transmission line formed by a superconducting Al film on a BaF_2 substrate. Cross strips formed Al–Al oxide–Al tunnel junctions that were used to study the effect of microwaves on the superconducting properties of the Al films. Large increases in the energy gap and transition temperature were observed for frequencies near 3.7 GHz. The enhancements were negligible below 1 GHz. Anomalous behavior of the features in the tunneling characteristics was observed above 5 GHz.

PACS numbers: 74.30.Gn, 73.60.Ka, 74.50.+r

The effect of microwave radiation on superconductivity has been of considerable experimental and theoretical interest, and also of some controversy, in recent years. Microwave enhancement of superconductivity has been reported in several manifestations: critical-current (I_c) and transition-temperature (T_c) enhancement in Al microbridges, point contacts, and narrow strips[1-3]; order-parameter enhancement in Al cylinders,[4] and energy-gap (Δ) enhancement in Al tunnel junctions.[5] Existing theories predict such enhancements as a consequence of a redistribution of quasiparticles away from the gap edge[6,7] and a reduction in the number of quasiparticles[7] in a superconductor irradiated with microwaves. Theoretical explanations of I_c enhancement without gap enhancement have also been proposed.[8-10] The quasiparticle redistribution theories[6,7] receive strong experimental support from the direct observation of gap enhancement via tunneling and from T_c enhancement in strips.[10] However, it was suggested in a recent communication that observations interpreted as T_c enhancement should instead be interpreted as I_c enhancement.[11]