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Investigation of the Energy-Level Scheme of Gd^{+3} in CaF_2 using Thermoluminescence*

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The energy-level scheme of Gd^{+3} in CaF_2 is investigated using thermoluminescent techniques. A large number of emission lines is found in the thermoluminenence spectrum. This large number of lines is attributed to different site spectra. The effect on the emission spectra of heat treatment and different origins of crystals is shown. The differences in spectra between samples result from the variations in abundance of the various rare-earth ion sites. This abundance is primarily determined by growth conditions and impurity concentrations.

INTRODUCTION

THERMOLUMINESCENCE has been used extensively to identify trapping levels in various crystals.[1] However, relatively few conclusions have been drawn as to the nature of the luminescent centers, because in most phosphors the emission spectrum consists of a small number of broad bands. In rare-earth-doped crystals, however, the thermoluminescent spectrum does provide information about the luminescent centers, because the emission spectrum consists of discrete lines characteristic of the rare earth.

Rare-earth-doped CaF_2 has been the subject of many investigations,[2] only some of them concerned with the thermoluminescence of these materials. Some conflicting results appear in the literature, and one must be aware of the fact that the amounts of impurities, and growth conditions, may have a great effect on the thermoluminescent glow and its emission spectrum.[3] The present work is concerned with the energy-level scheme of Gd^{3+} in a CaF_2 matrix, using thermoluminescence. It will be evident that in general the thermoluminescent spectrum even at low temperatures (77°K) may consist of various site-emission spectra. This seems to be in some conflict with the conclusions of Kiss and Staebler,[4] based on their studies of CaF_2:Dy^{3+}; on the other hand, our results seem to be consistant with those of Makovsky concerning fluorescence in CaF_2: Gd^{3+}.[5]

EXPERIMENTAL

The crystals used in the present work were obtained from two sources: (a) from the Harshaw Chemical Company (the concentration of Gd in these crystals is unknown, but it is estimated to be 0.05%); (b) from J. Merz[6] (the concentration of Gd is thought to be about 0.1%). Cleaved crystals, of approximately 8×5×2 mm, were x irradiated with a 20-kV-peak 10-mA copper tube, typically for 30 min at 77°K, inside a vacuum cryostat with fused silica windows. The general glow curve and the spectral distribution of the glow were taken simultaneously in the following way: A photomultiplier, IP28, was placed at one window of the cryostat, to allow the total glow to be recorded. The opposite window of the cryostat was brought to nearest access to the entrance slit of a Hilger medium-resolution quartz spectrograph ($\simeq$2 Å in the wavelength region of 3100 Å); between glow peaks the photographic plate was moved so that the spectral distribution of each glow peak was recorded separately.

RESULTS

Figure 1 shows the general glow curves of CaF_2: Gd^{3+} between 100 and 300°K. Figure 1(a) shows the results given by the Harshaw crystal after x irradiation at 77°K for 30 min. Figure 1(b) shows the results given by the same crystal, after it had been heated to 830°C in about 2 h, and cooled to room temperature in about 1 h. During this heat treatment, the crystal was open to the atmosphere. Figure 1(c) is the glow curve obtained from the crystal supplied by J. Merz. The heating rate in all these measurements was 11 deg/min. The arrows in these figures indicate the temperatures at which the photographic plate was moved so as to obtain a separate spectral distribution for each of these temperature intervals. The letters indicate those peaks whose activation energies have been calculated—see Table I.

Several methods for the analysis of glow peaks have been proposed.[7] Activation energies of some of the glow peaks are given in Table I, and have been computed

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[1] M. Schlesinger, J. Phys. Chem. Solids **26**, 1761 (1965).

[2] See for references J. Merz, Harvard University, Division of Engineering and Applied Physics Technical Report No. 514 (unpublished).

[3] I. V. Stepanov and P. P. Feofilov, Dokl. Acad. Nauk SSSR **108**, 615 (1956) [English transl.: Soviet Phys.—Doklady **1**, 350 (1956)]. These authors show the influence of the reduction-oxidation conditions under which the crystals are grown on their optical spectra.

[4] Z. J. Kiss and D. L. Staebler, Phys. Rev. Letters **14**, 691 (1965).

[5] J. Makovski, Phys. Letters **19**, 647 (1966).

[6] We are indebted to Dr. J. Merz (current address, Bell Telephone Laboratories) and Professor P. S. Pershan for making some of their crystals available to us. These were grown by Dr. Merz during his doctoral research at the Gordon McKay Laboratory of Harvard University. Although the crystals were grown under similar conditions to the ones he actually measured, these were not, in fact, the same crystals he reported on. (Reference 2). As a consequence, direct comparison of his results and the ones presented here may perhaps not be justified.

[7] K. H. Nicholas and J. Woods, Brit. J. Appl. Phys. **15**, 783 (1964).

from the formula

$$E=kT_g^2/\delta,$$

where E is the activation energy, k is Boltzmann's constant, T_g is the temperature of the glow peak maximum, and δ is the high-temperature half-width of the glow peak (i.e., δ equals T_2-T_g, where T_2 is the temperature at half-intensity on the high-temperature side of the peak[8]). No special attempts have been made in this work to further elucidate the nature of the trapping sites. Although comparison of the glow curves in Fig. 1 shows that the glow peaks do not necessarily occur at identical temperatures, it seems reasonable to assume that these sites are charscteristic of the host lattice—this will be discussed further in the next section.

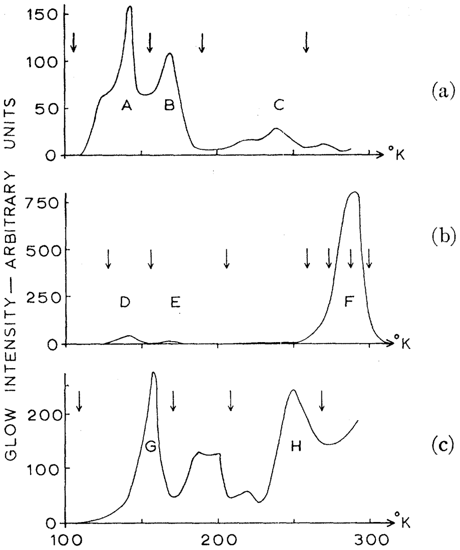

FIG. 1. General glow curves of $CaF_2:Gd^{3+}$ x-irradiated for 30 min at 77°K. (a) Harshaw crystal, untreated. (b) Same crystal as in 1(a) after being heated to 830°C in open air. (c) Crystal supplied by J. Merz, untreated. In all cases the heating rate was 11 deg/min. The arrows indicate the temperatures at which the spectroscopic plate was moved. The capital letters indicate those peaks whose acitvation energies have been calculated—see Table I.

The thermoluminescent emission spectrum is characteristic of the rare earth, and examples thereof are shown for Gd in Figs. 2, 3, 4, and 5. Figure 2 is the microdensitometer trace of the emission spectrum from one of the main glow peaks [peak A, Fig. 1(a)] of the Harshaw crystal, prior to heat treatment. Identical traces have been obtained for all the glow peaks whose spectral distribution we have been able to record.

Figure 3 is the microdensitometer traces of the emission spectra from the main glow peaks of the Harshaw crystal, after heat treatment at 830°C. Figures 3(a), 3(b), and 3(c) correspond to the temperature intervals 125–150°K, 275–285°K, and 285–300°K, respectively. Comparison of Figs. 2 and 3 reveals that additional emission lines appear after heat treatment.

TABLE I. Activation energies in some glow peaks of $CaF_2:Gd^{+3}$.

Crystal	Peak (see Fig. 1)	T_g (°K)	Activation energy (eV) ±10%
Harshaw untreated	A	143	0.42
	B	170	0.52
	C	240	0.73
Harshaw heat-treated to 830°C	D	141	0.40
	E	170	0.48
	F	289	0.85
Merz's crystal	G	158	0.57
	H	251	0.51

Figure 4 is the microdensitometer trace for the emission of the crystal supplied by J. Merz. Figures 4(a), 4(b), and 4(c) correspond to the temperature intervals 110–170°K, 170–210°K, and 210–270°K, respectively.

Figure 5 shows an additional group of emission lines, observed *only* in Merz crystal, in the wavelength region 2700–2800 Å. The temperature intervals for Figs. 5(a), 5(b), and 5(c) are identical with those for Figs. 4(a), 4(b), and 4(c), respectively.

ANALYSIS OF RESULTS AND DISCUSSION

The rare earth, believed to enter the CaF_2 lattice substitutionally for the Ca^{2+}, seems to be more stable in the 3+ state.[4,9,10] This requires some charge compensation; a number of such mechanisms can occur, which may differ from each other in their degree of symmetry.[5] Upon x irradiation the rare earth is reduced to the 2+ state, while the hole is trapped in a nearby site probably characteristic of the host lattice. Upon heating, the trapped hole is released and recombines with the extra electron on the rare earth, reoxidizing it to an excited 3+ state. The rare-earth 3+ returns to its ground state, thus emitting its characteristic radiation. The presently available optical and ESR data[2] seem to be in fair agreement with this model, and it is for this reason that one expects the thermoluminescent

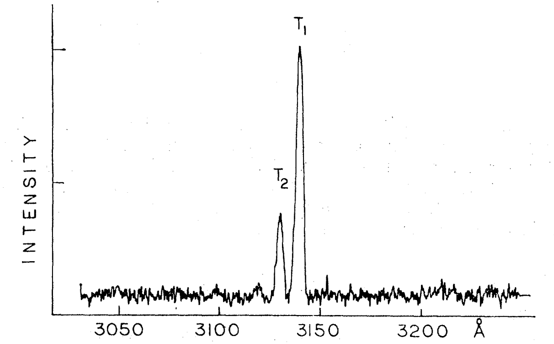

FIG. 2. The microdensitometer trace of the emission spectrum of one of the main glow peaks [peak A, Fig. 1 (a)] in the untreated Harshaw crystal. Identical results were obtained for all the other glow peaks in this crystal.

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[8] A. Halperin and A. A. Braner, Phys. Rev. **117**, 408 (1960).

[9] W. Hayes and J. W. Twidell, J. Chem. Phys. **35**, 1521 (1961).

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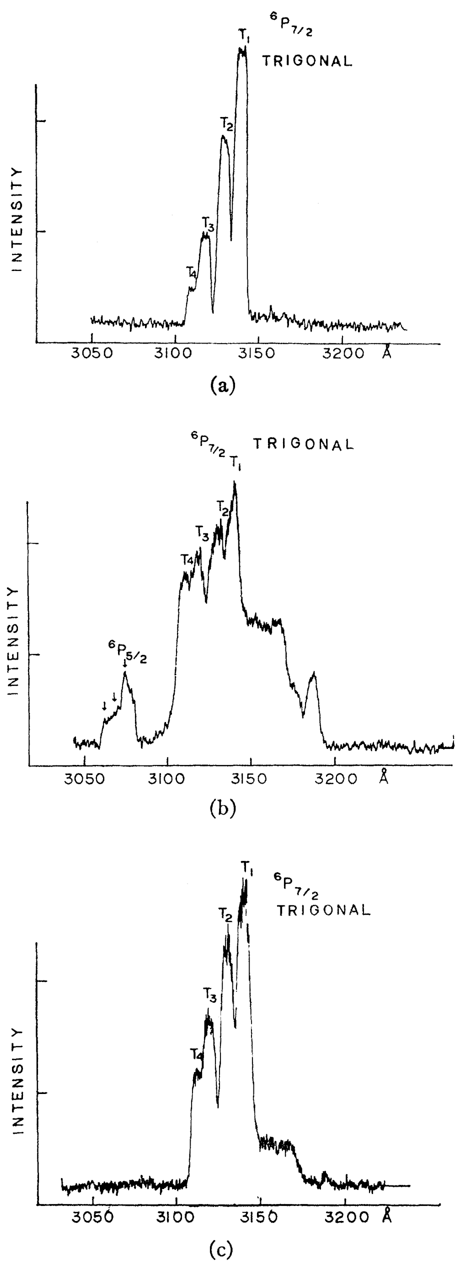

FIG. 3. Microdensitometer traces of the emission spectrum from glow peaks of the Harshaw crystal after heating. (a) The spectrum in the temperature range 125–150°K—peak D, Fig. 1(b). (b) The spectrum in the temperature range 275–285°K—first half peak F, Fig. 1(b). (c) The spectrum in the temperature range 285–300°K—second half peak F, Fig. 1(b).

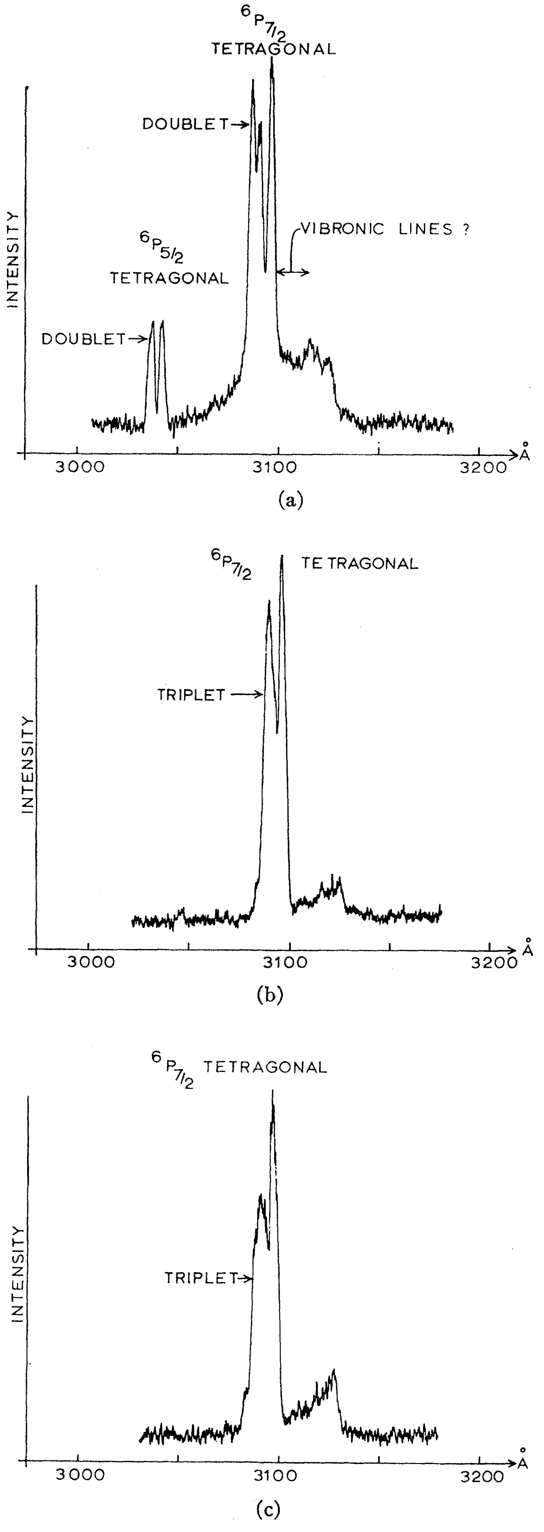

FIG. 4. Microdensitometer traces of the emission spectrum from glow peaks of Merz's crystal—untreated—in the 3100 Å region. (a) Spectrum in the temperature range 110–170°K—peak G, Fig. 1(c). (b) Spectrum in the temperature range 170–210°K. (c) Spectrum in the temperautre range 210–270°K—peak H, Fig. 1(c).

emission to be due to transitions within the rare-earth 3+ ion.

The electron configuration of Gd^{3+} is $4f^7$; the ground state $^8S_{7/2}$ is orbitally nondegenerate. The crystal-field splitting of this ground state is about 2 cm^{-1}, which is too small to be resolved in our measurements, and therefore the observed splittings are due to the crystal-field splittings of the excited states. These facts make this ion relatively simple to analyze compared to other rare-earth ions. The first excited state of Gd^{+3} is $^6P_{7/2}$ at 3.20×10^4 cm^{-1} ($\simeq$3100 Å) above the ground state[11]; the second excited state is $^6P_{5/2}$ at about 3050 Å.

Inspection of Figs. 3(a), 3(b), and 3(c) reveals the existence of four main lines, indicated by T_1 through T_4. These are believed to be due to the $^6P_{7/2}$-$^8S_{7/2}$ transition split by a trigonal field; a possible charge compensation in this case is by O^{2-} at a lattice fluoride site. This identification is in parallel to the "T" site spectra as labeled by Makovski.[5] In the untreated Harshaw crystal, Fig. 2, only the lines T_1 and T_2 appear. Heating the crystal in air might possibly increase the oxygen content of the crystal,[12] thus increasing the intensity of the lines T_3 and T_4, as is observed in Fig. 3. The group of lines, [Fig. 3(b)] at about 3070 Å conforms with the $^6P_{5/2}$-$^8S_{7/2}$ transition split by the same trigonal field.[5,11]

In Fig. 4, Merz's crystal, the emission at about 3100 Å is identified again as the $^6P_{7/2}$-$^8S_{7/2}$ transition, split this time by a tetragonal field,[5,11] with a possible charge compensation by an interstitial F^-. The line labeled "doublet" in Fig. 4(a) is believed to consist of two closely spaced lines. This symmetry corresponds to the "A" site spectra symmetry, as labeled by Makovsky.[5] The lines at about 3040 Å [Fig. 4(a)] are attributed to the $^6P_{5/2}$-$^8S_{7/2}$ transitions split by the same tetragonal field. Again we assume that line marked "doublet" composes two closely spaced components. We wish to point out that both the wavelengths and separations of the various lines are in reasonable agreement with those of Makovsky.[5] In both Figs. 3 and 4, there appears on the long-wavelength side of the main emission lines, a group of weak, unresolved components, which tend to diminish towards higher temperatures. This is most easily observed by comparing Figs. 4(a) and 4(c). As indicated in 4(a), we tentatively identify some of these as vibronic side bands. It is also to be noted that upon passing to higher temperatures, some of the various lines tend to broaden, and it becomes more difficult to resolve closely spaced lines. A careful study of the effect of an increase in temperature upon the various emission lines can provide useful information about the interaction between the impurity and the lattice. This kind of study, however, has not yet been carried out.

Figure 5, Merz crystal, represents a group of emission lines that should be attributed to ^6I-^8S transitions; again it seems premature to try and analyze this group of lines in detail. However, we may point out that (a) The wavelengths at which they occur leave no doubt that these are ^6I-^8S transitions[11] and (b) Makovsky, from his fluorescence studies, has pointed out that the ^6I levels of site A are strongly radiative, while those of site T are not so at all, in agreement with our results.

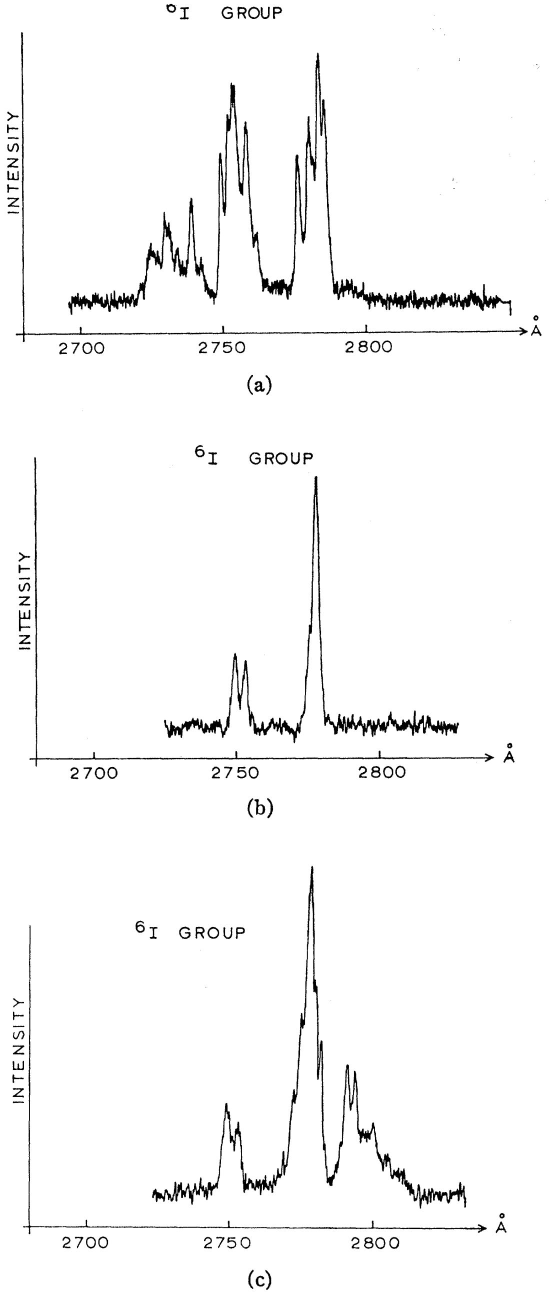

FIG. 5. Microdinsitometer traces of emission lines observed *only* in Merz's crystal, in the wavelength region 2750–2800 Å. (a) The spectrum in the temperature range 110–170°K—peak G, Fig. 1(c). (b) The spectrum in the temperature range 170–210°K. (c) The spectrum in the temperature range 210–270°K-peak H, Fig. 1(c).

In the course of the present work the Russell-Saunders coupling scheme has been used to describe the various spectra. The actual situation is best described by a scheme intermediate between L-S and j-j. The former is widely used, however, for reasons of convenience.

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In conclusion, the present work shows that different site spectra may appear in $CaF_2:Gd^{3+}$ crystals, which have been grown in different ways. The effect of heat treatment was also demonstrated. These results seem to rule out generalizations such as those made by Kiss and Staebler,[4] according to which in all CaF_2 doped with rare earths, the thermoluminescence is due to rare earth in cubic sites only. On the other hand, our results seem to be parallel to those of Makovsky,[5] who studied the fluorescence of this material. As for the general glow curve, the various glow peaks do not seem to appear at identical temperatures in different crystals. Nevertheless, one is tempted to assume that the trapping sites are characteristic of the host lattice, as is the case in the alkali halides.[13] Since our proposed mechanism for the thermoluminescence would assume these sites to be in close proximity to the rare earth, it is not unexpected then that these sites are influenced by the different symmetries surrounding the rare earths, thus causing changes in activation energies from crystal to crystal.

Finally, it is intended to extend the present work to CaF_2 doped with other rare earths.

ACKNOWLEDGMENT

We wish to thank Dr. H. I. S. Ferguson for the loan of optical equipment used in this investigation.

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Positron Annihilation in Real Metals. II. Calculation of Core Enhancement Factors*

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A first-principle calculation of core-annihilation enhancement factors in sodium and aluminum is presented. The computations are based on a previously developed theory whose numerical results had formerly been only crudely estimated. The core electrons are treated in the tight-binding approximation using atomic wave functions appropriate to the metallic state. The conduction-band states are taken to be single orthogonalized plane waves. The central core-conduction matrix element of the theory is evaluated with one computational approximation: a simplifying angular average. The enhancement factors obtained have a weak momentum dependence, so the shape of the core contribution calculated without correlations is unaffected. The enhanced contribution of the orthogonalization parts of *conduction*-electron wave functions remains to be evaluated, so that comparison of our results with experiment is not completely unambiguous. With this reservation, however, the agreement on the whole is satisfactory for both distributions and total lifetimes.

I. INTRODUCTION

IN a previous paper[1] a theory of positron annihilation was derived, which included band-structure effects while accounting partially for correlation effects between the annihilating electron-positron pair. The work was based on a summation of a select infinite subset of Feynman graphs in the perturbation expansion of the electron-positron Green's function. It is a space-time contraction of this two-body Green's function which determines the annihilation rate in a nonrelativistic system of electrons and positrons. The graphs summed were the ladder diagrams; this approximation was originally introduced, with considerable success, by Kahana[2] in a discussion of lifetimes in an electron gas. Since then it has been analyzed more critically by Carbotte and Kahana[3] and refined by Bergersen[4] and by Carbotte.[5] These refinements of electron-gas theory will not concern us directly here (we will return to them briefly in the last section). They represent only secondary corrections to the main ladder contribution. Also, electron-gas results cannot be taken over directly to the case of core electrons. More important, the ladder graphs have not, as yet, been properly evaluated for core electrons although from the crude estimate supplied in Ref. 1 they are known to give important corrections to the independent-particle model (I.P.M.) extensively used in past discussions of this problem.[6–8] The purpose of this paper is to carry out a computation of ladder corrections.

It is not difficult to understand, at least in a general way, the relevance of the ladder approximation to the calculation of lifetimes. The first point to realize is that for an arbitrary system of low-energy electrons and

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* Research supported by the National Research Council of Canada.

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