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Lowest $4f \rightarrow 5d$ Transition of Trivalent Rare-Earth Ions in CaF_2 Crystals

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The lowest $4f \rightarrow 5d$ ultraviolet absorption band of eleven (Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, and Yb) of the fourteen trivalent rare-earth (RE) ions in host CaF_2 crystals has been measured. The room temperature absorption cross section [cm^2] and half-width [cm^{-1}] of these bands for the first-half series of RE^{3+} are larger than that of the second-half series (from Tb^{3+} on), possibly because of some spin-forbiddenness in the transition of the latter. Typically, they are $\sim 5\times 10^{-18}$ cm^2 and ~ 1700 cm^{-1}, respectively, for the former and $\sim 3\times 10^{-18}$ cm^2 and ~ 1300 cm^{-1}, respectively, for the latter at typical concentration of $\sim 10^{-4}$. The oscillator strength is estimated to be $\sim 10^{-2}$ for the first half-series and $\sim 4\times 10^{-3}$ for the second half-series RE^{3+}. At liquid nitrogen temperature the band sharpens and shifts ~ 200 cm^{-1} toward lower wave number, probably because of increasing crystal field in the contracted lattice; a zero-phonon line and some vibrational structure are also developed in Ce^{3+}- and Pr^{3+}-doped CaF_2. The location of the band ranges from $\sim 33\,000$ cm^{-1} (Ce^{3+}) to $\sim 71\,000$ cm^{-1} (Yb^{3+}), with that of Gd^{3+} and Lu^{3+} outside ($\gtrsim 80\,000$ cm^{-1}) of the transparent region of CaF_2 crystal. Compared with the data available for the free ions Ce^{3+}, Pr^{3+}, and Yb^{3+}, the location of the lowest $4f \rightarrow 5d$ transition of $(RE)^{3+}$ ions in CaF_2 is found to be lowered $\sim 18\,000$ cm^{-1} in the crystal environment. The energy of the lowest $4f \rightarrow 5d$ transition is described satisfactorily by a formula due to Jørgensen for $4f^n \rightarrow 4f^{n-1}\,5d$ transitions in the free ion, decreased by $18\,000$ cm^{-1}.

As a direct approach to the problems involving configurations higher than $4f^n$, we have measured the ultraviolet absorption spectra of the triply ionized rare earths Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu in CaF_2 host crystals in the spectral region up to the intrinsic absorption edge of the host at $\sim 80\,000$ cm^{-1} (~ 1250 Å). In this paper we report our data on the lowest observed $4f \rightarrow 5d$ transition. We describe first the general characteristics of this band and the variation of the wave number of this band with the number of f-shell electrons of the RE^{3+} ion. Experimental data are compared with both experimental and calculated values of the transition energies in free RE^{3+} ions. The comparison shows a fair correlation between the experimental data for RE^{3+} ions in CaF_2 and the results of the free ion calculations, which include various interelectronic energies between $4f$ electrons but neglect the electrostatic interaction between $5d$ and $4f$ electrons. However, the lowest bands due to $4f \rightarrow 5d$ transitions in the crystal are consistently lower than expected from the free ion calculations by approximately $18\,000$ cm^{-1}. This difference is due to the crystal field lowering of the ground state of the $4f^{n-1}\,5d$ configuration. Since the calculated free ion energies compare reasonably well with the limited free-ion data available,[1] the crystal data may be useful for estimating the energy of the $4f^{n-1}\,5d$ configuration in cases where free--ion data is not yet available.

The lowest of the strong ultraviolet absorption bands attributed to $4f^n \rightarrow 4f^{n-1}\,5d$ transitions in RE^{3+} ions in CaF_2 are shown in Fig. 1. Table I summarizes the room-temperature data for these bands, giving wave number, absorption cross-section and half-width. The typical rare-earth ion concentration used for measurement is $\sim 10^{-4}$ mole fraction. The wave number of the lowest $4f \rightarrow 5d$ line ranges from $32\,500$ cm^{-1} for Ce^{3+} to $70\,700$ cm^{-1} for Yb^{3+}. The bands of Gd^{3+} and Lu^{3+} are not observed because they are greater than $\sim 80\,000$ cm^{-1}, the cutoff of CaF_2. Table I shows that the absorption cross-section and the half-width of the lowest $4f \rightarrow 5d$ bands for the first half-series of RE^{3+} are larger than for the second half-series (from Tb^{3+}), possibly because of some spin-forbiddenness in the transition of the latter.[2,3] Typically, they are $\sim 5\times 10^{-18}$ cm^2 and ~ 1700 cm^{-1}, respectively, for the first half-series, and $\sim 3\times 10^{-18}$ cm^2 and ~ 1300 cm^{-1}, respectively, for the second half-series. The estimated oscillator strengths are therefore $\sim 10^{-2}$ and $\sim 4\times 10^{-3}$, respectively, for the two half-series. At liquid nitrogen temperature the $4f \rightarrow 5d$ bands sharpen and shift ~ 200 cm^{-1} toward lower wave number, presumably due to increasing crystal-field strength in the contracted lattice. A zero-phonon line and some vibrational structure[4] with separations of 100 to 200 cm^{-1} appear in Ce^{3+} and Pr^{3+}-doped CaF_2 crystals,[5] as shown by the fine-line curves in Fig. 1. The $4f \rightarrow 5d$ band appears as a structureless band at room temperature even at 10^{-5} mole fraction of RE^{3+}.

There are three irregularities that appear in the lowest $4f \rightarrow 5d$ absorption bands of RE^{3+} in CaF_2: First, the lowest $4f \rightarrow 5d$ band of Ho^{3+} at $64\,000$ cm^{-1} has an absorption cross section less than half that of the neighboring Dy^{3+} and Er^{3+}. On the other hand, the next

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[1] Ce^{3+} [R. J. Lang, Can. J. Res. **14A**, 127 (1936)]; Pr^{3+} [J. Sugar, J. Opt. Soc. Am. **55**, 1058 (1965); H. M. Crosswhite, G. H. Dieke, and Wm. J. Carter, J. Chem. Phys. 43, 2047 (1965)]; Yb^{3+} [B. W. Bryant, J. Opt. Soc. Am. **55**, 771 (1965)].

[2] D. S. McClure and Z. Kiss, J. Chem. Phys. **39**, 3251 (1963).

[3] C. K. Jørgensen (private communication).

[4] M. H. Crozier reported sharp lines in 10^{-6} Ce^{3+} (Ref. 8) and 10^{-6} Pr^{3+} [Bull. Am. Phys. Soc. **9**, 631 (1964)] doped CaF_2 crystals at liquid-helium temperature.

[5] In Nd^{3+}, Tb^{3+}, and Dy^{3+} doped CaF_2 crystals the low-temperature structure is not as well developed as Ce^{3+}- and Pr^{3+}-doped CaF_2. For the other RE^{3+} ions the lowest $4f \rightarrow 5d$ bands are in the region of the line spectrum of our source and it is therefore difficult to resolve low-temperature absorption structure.

TABLE I. The lowest $4f \rightarrow 5d$ band of trivalent rare earths in CaF$_2$ crystal at room temperature.

Rare earth ion	Ground state of $4f^n$ configuration	Concentration in mole fraction %	Energy of the lowest $4f \rightarrow 5d$ transition 1000 cm^{-1}	Absorption cross-section 10^{-18} cm^2	Half-width toward low wave number cm^{-1}
Ce^{3+}	$4f^1\,{}^2F_{5/2}$	0.01	32.5	3.9	1400
Pr^{3+}	$4f^2\,{}^3H_4$	0.015	45.6	5.5	1700
Nd^{3+}	$4f^3\,{}^4I_{9/2}$	0.02	55.9	5	1700
Pm^{3+}	$4f^4\,{}^5I_4$	Not available			
Sm^{3+}	$4f^5\,{}^6H_{5/2}$	0.01	59.5	5.5	1800
Eu^{3+}	$4f^6\,{}^7F_0$	0.006	68.5	4.2	1400
Gd^{3+}	$4f^7\,{}^8S$	0.001–10	>78		
(Tb^{4+}	$4f^7\,{}^8S$	<0.02	75.4	>1.16[a]	800)
Tb^{3+}	$4f^8\,{}^7F_6$	0.02	46.5	2.7	1300
Dy^{3+}	$4f^9\,{}^6H_{15/2}$	0.01	58.9	2.8	1400
Ho^{3+}	$4f^{10}\,{}^5I_8$	0.01	64.1	1.2	1100
			(68)	(6.4)	(1400)
Er^{3+}	$4f^{11}\,{}^4I_{15/2}$	0.01	64.2	2.75	1100
Tm^{3+}	$4f^{12}\,{}^3H_6$	0.01	64	3.74	1400
Yb^{3+}	$4f^{13}\,{}^2F_{7/2}$	0.01	70.7	3.2	1200
Lu^{3+}	$4f^{14}$	0.1	>80		

[a] This value is calculated by assuming the concentration of Tb^{4+} equal to that of Tb^{3+}, 0.02%.

higher $4f \rightarrow 5d$ band of Ho^{3+} at 68 000 cm^{-1}, as shown in Fig. 1 and listed in Table I in parentheses, has a cross section more than twice that of the neighbors. Second, in the absorption spectra of Sm^{3+}($4f^5$), Eu^{3+}($4f^6$) and Yb^{3+}($4f^{13}$) the lowest $4f \rightarrow 5d$ band has twin peaks with separations of approximately 1000, 3000, and 2000 cm^{-1}, respectively. Possible sources of these twin peaks are (1) the likely presence of the corresponding doubly ionized rare-earth ion RE^{2+} or (2) the structure of $4f^{n-1}$ electrons (${}^5I$ or $4f^4$, ${}^6H$ or $4f^5$, and ${}^3H$ of $4f^{12}$) in the $4f^{n-1}\,5d$ configuration.[3] Third, in the absorption spectrum of Tb^{3+} in CaF$_2$, there is an absorption band at ~75 400 cm^{-1}, shown in Fig. 1 and listed in Table I in parentheses, resembling the typical lowest $4f \rightarrow 5d$ peak of (RE)$^{3+}$ in CaF$_2$. This peak may be the lowest $4f \rightarrow 5d$ transition of Tb^{4+} ($4f^7$) in CaF$_2$. Tb^{4+} might be present in the Tb^{3+}-doped CaF$_2$ (see for example Ref. 2).

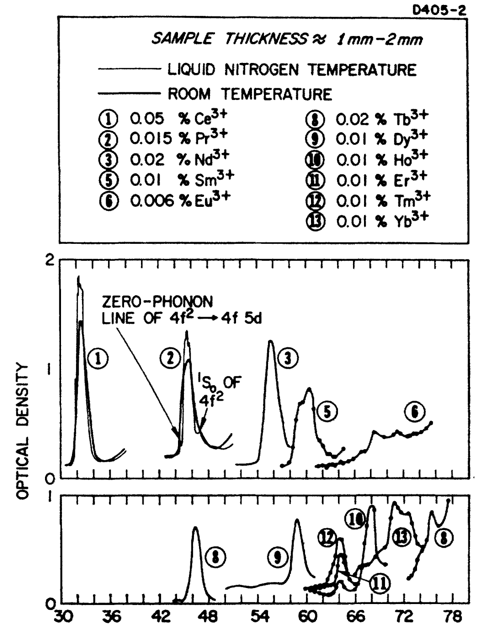

FIG. 1. Lowest $4f \rightarrow 5d$ absorption band of trivalent rare-earth ions in CaF$_2$ crystals at room temperature. (For Ce^{3+} and Pr^{3+} also at liquid-nitrogen temperature.)

The variation of the wave number of the lowest $4f \rightarrow 5d$ transition of RE^{3+} with RE ion has been investigated by several authors. Dieke and Crosswhite[6] have given a survey of the $4f^{n-1}\,5d$ configuration of the free RE^{3+} and RE^{2+} ion gased on preliminary empirical data and approximate calculations. Jørgensen[7] has formulated the lowest energy of transition of both $4f^n \rightarrow 4f^{n-1}\,5d$ and $4f^n \rightarrow 4f^{n+1}$ (electron transfer) in terms of spin-pairing energy and stabilization effects in the $4f^n$ configuration. By comparing his calculated results for both $4f^n \rightarrow 4f^{n-1}\,5d$ and $4f^n \rightarrow 4f^{n+1}$ with experimental data he confirmed the distinction between the broad electron transfer band and the relatively narrow $4f \rightarrow 5d$ transition peak of lanthanide (RE^{3+}) complexes. Crozier[8] has also made a similar calculation on the variation of the lowest $4f \rightarrow 5d$ transition with (RE^{3+}) ion in CaF$_2$. Both Jørgensen and Crozier assumed the electrostatic interaction between $5d$ and $4f$ electrons is not importnt. For (RE)$^{2+}$ in CaF$_2$, McClure and Kiss[2] have measured the $4f \rightarrow 5d$ spectra. They compared[2] the observed onset of the $4f^n \rightarrow 4f^{n-1}\,5d$ transition of (RE)$^{2+}$ with the value calculated from their formula, which included mainly the difference between the energy of a $5d$ electron interacting with $n-1$ $4f$ electrons and the energy of a $4f$ electron interactiong with $n-1$ $4f$ electrons, by matching the energy of transition at a "typical" (RE)$^{2+}$ ion, Sm^{2+}. The agreement is good except for anomalies for La^{2+}, Ce^{2+}, Gd^{2+}, and

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[6] G. H. Dieke and H. M. Crosswhite, Appl. Opt. **2**, 675 (1963).

[7] C. K. Jørgensen, Mol. Phys. **5**, 271 (1962); and a paper represented at the Fifth Rare-Earth Research Conference, Ames, Iowa, 1965 (unpublished).

[8] M. H. Crozier, Phys. Rev. **137**, A1781 (1965).

Tb^{2+}, which probably occur because[2] the lowest crystal-field component of $4f^{n-1}\,5d$ is at or near the ground state of $(RE)^{2+}$ in CaF_2.

Compared with different types of samples employed in the literature[2,6,7,9,10] $(RE)^{3+}$ ions in CaF_2 crystals present a simple system for studying the variation of the wave number of the lowest $4f^n \rightarrow 4f^{n-1}\,5d$ transition. It is expected to be simple because of the high degree of ionization of $(RE)^{3+}$, the large electronegativity of the host lattice fluorine ions, and the practical convenience of measuring solid samples. The large nuclear charge in the highly ionized $(RE)^{3+}$ separates the ground $4f^n$ state well below the $4f^{n-1}\,5d$ configuration.[6] This large interconfigurational separation prevents the possible occurrence of the anomalies noted in the case of La^{2+}, Ce^{2+}, Gd^{2+}, and Tb^{2+} in CaF_2.[2] For example, the lowest $4f \rightarrow 5d$ energy of $(RE)^{3+}$ in CaF_2 is generally more than 20 000 cm^{-1}, which is about the magnitude of the crystal field strength and considerably higher than the $4f \rightarrow 5d$ energy of $(RE)^{2+}$ in CaF_2 (Ref. 2). The large electronegativity of the host ion fluorine places the wave number of the electron transfer transition higher than that of the $4f \rightarrow 5d$ transition. The electron transfer energy in fluorides may be $\sim$25 000 cm^{-1} higher than in oxides.[3] Solid samples, especially single crystals, are usually more stable than liquid solutions and for a general survey of the trend of the lowest $4f \rightarrow 5d$ energy energy of $(RE)^{3+}$ as reported here, absorption or excitation measurements on solids are less complicated experimentally than emission measurements from free ions.

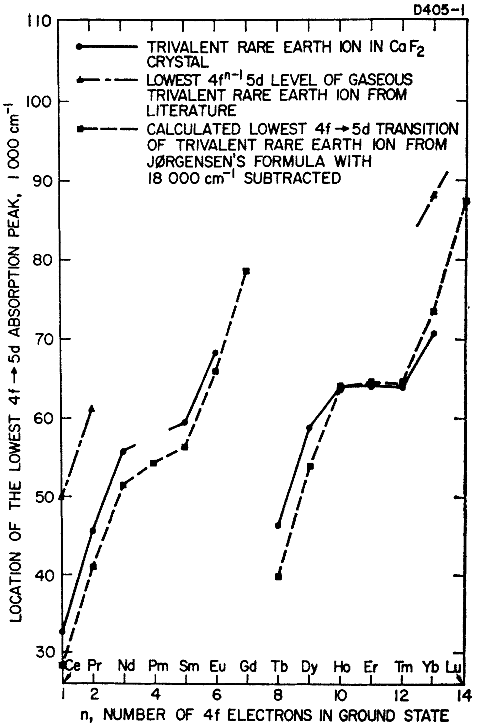

FIG. 2. Variation of the energy of the lowest $4f \rightarrow 5d$ transition of trivalent rare-earth ions through the rare-earth series.

The variation of the wave number of the lowest $4f \rightarrow 4f^{n-1}\,5d$ of RE^{3+} with RE ion is shown in Fig. 2, where the rare earths are plotted in order of increasing number of f electrons. There are three sets of data. The experimental data are the locations of the lowest $4f \rightarrow 5d$ absorption peaks at room temperature as shown in Fig. 1. Free ion data available in the literature[1] for the lowest $4f^{n-1}\,5d$ level of gaseous Ce^{3+} Pr^{3+}, and Yb^{3+} are also plotted. The data of $(RE)^{3+}$ in CaF_2 are about 18 000 cm^{-1} lower than the corresponding free ion data. A substantial portion of this lowering in energy is presumably due to the crystal-field splitting of $4f^{n-1}\,5d$ level in CaF_2. Calculated data obtained from Jørgensen's formula[7]

$$W_2 + (n-1)(E-A)_2 + k_4 D + k_5 E^3 + k_6 \zeta_{4f} \qquad (1)$$

for the wave number of the lowest $4f^n \rightarrow 4f^{n-1}\,5d$ transitions in the free ion, but decreased by 18 000 cm^{-1}, are also plotted in Fig. 2. According to Jørgensen,[7] the first term W_2 in Eq. (1) is a reference for comparison within a given series, where n, the number of f electrons, is varied; for example $W_2 = 45\,000$ cm^{-1} for gaseous $(RE)^{3+}$. The coefficients $(n-1)$, k_4, k_5, and k_6 in the other terms of Eq. (1) are determined from the number of $4f$ electrons of $(RE)^{3+}$, n. The second term describes the stabilization of the $4f^n$ orbital; $(E-A)_2$ indicates that the gradually increasing stabilization of the $4f$ orbital energy can be written as the difference between the increase of the core attraction E and the increase (of the type F^0) of interelectronic repulsion A in the $4f$ shell; $(E-A)_2 = 5000$ cm^{-1} for gaseous $(RE)^{3+}$. The third term is a spin-pairing energy with D being the spin-pairing energy parameter. As with all other interelectronic repulsion parameters, D is proportional to the average value of the reciprical radius $\langle r^{-1} \rangle$ of the partly filled $4f$ shell and is determined from data for $4f^n \rightarrow 4f^n$ transitions; $D = 6700$ cm^{-1} for free $(RE)^{3+}$ ions. Values of k_4 make the spin-pairing energy increase linearly with n except for a sudden drop of $(96/13)D$ after the completion of the fist half-shell at $n=7$. The fourth term, $k_5 E^3$, takes into account the stabilization of H- and I-ground terms relative to the spin-pairing energy term by amounts proportional to Racah's parameter for interelectronic repulsion, E^3; values of k_5 make the curves flat around $n=4$ and $n=11$, hence producing the "double S curve,"[3] as shown in Fig. 2. The fifth term, $k_6 \zeta_{4f}$, considers the stabilization due to relativistic effects, which are expressed to a first approximation by a multiple of the Landé parameter ζ_{4f}; values of k_6 vary with n in the opposite manner to that of k_4 and hence they make the curves in Fig. 2 less steep. E^3 and ζ_{4f} for each $(RE)^{3+}$ are well known[6,7] from the data for $4f^n \rightarrow 4f^n$ transitions.

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[9] C. K. Jørgensen, *Absorption Spectra and Chemical Bonding in Complexes* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1962).

[10] For example, C. K. Jørgensen, R. Pappalardo, and E. Rittershaus, Z. Naturforsch. **20a**, 54 (1965) and references therein.

The correlation, shown in Fig. 2, between the data for $(RE)^{3+}$ ions in CaF_2 and the calculated free ion data, decreased by 18 000 cm^{-1}, suggests that the variation of the location of the lowest $4f \rightarrow 5d$ transition of $(RE)^{3+}$ ions in crystals[11] containing anions of large electronegativity is simply like that of free ions. This correlation between the free ion and ion-in-crystal data may be useful in predicting the location of the lowest $4f^{n-1}\,5d$ level of free $(RE)^{3+}$ ions not yet observed experimentally.

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[11] Our preliminary data on $(RE)^{3+}$ in SrF_2 and BaF_2 crystals are similar to those in CaF_2 with corresponding reduction in energy ~17 000 cm^{-1} for host SrF_2 and ~16 000 cm^{-1} for host BaF_2. For the host LaF_3 crystals, the present progress in purifying the crystal and hence in extending its transparent region toward vacuum ultraviolet will allow a similar measurement in the near future [Hugh M. Muir and Wm. Stein in a paper presented at Fifth Rare-Earth Research Conference, Ames, Iowa, 1965 (unpublished); M. Robinson and D. M. Cripe (to be published)].

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Simple Model for Collision Effects in Photoemission

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We treat the problem of energy loss to phonons in photoemission by making a one-dimensional approximation. We include pair creation and finite electron reflectivity at the surface. It is assumed that after pair creation neither primary nor secondary electrons can escape. Phonon scattering, pair creation, and reflectivity are assumed independent of electron energy, although this will often be a poor approximation. With the above approximations the problem is exactly soluble. For large phonon energy losses the results are similar to the predictions of age theory.

I. INTRODUCTION

PHOTOELECTRIC emission is potentially a very valuable tool for the study of the band structure of solids. The potential value of photoemission results from the richness of the measurements which are possible. Listed in order of progressive refinement these are total yield versus photon energy[1]; energy distribution of the yield at fixed photon energy[2]; and energy distribution of the yield at fixed photon energy and angle of emission.[3]

The above information is most readily interpretable in cases where the emitted electrons have suffered very little or no energy loss in the process of escaping from the solid.

In order to obtain the most reliable interpretation of the experimental data, however, a detailed knowledge of the energy-loss processes is necessary.

In the present paper we study a simple one-dimensional model in which we can allow for the effects of pair-creation scattering, phonon scattering, and finite reflection at the surface in a way which leads to an exactly soluble result for the total probability of escape and for the energy distribution of the emitted electrons assuming a delta-function initial energy.

We assume throughout that if an electron undergoes pair creation, neither the scattered primary nor the secondaries can escape. Clearly this assumption is valid only for electrons within a few volts of the vacuum potential.

The three-dimensional case has been studied in considerable detail by Baraff.[4] He has shown that simple results for the energy-distribution function of degraded electrons may be obtained using the approximations of neutron age theory. The age-theory approximation is good when phonon energy losses are large so that the energy-distribution function can be assumed to be a continuous function of the number of phonon-scattering events. Age theory also makes simplifying assumptions about the angular dependence of the distribution function. Naturally, our one-dimensional approximation amounts to an even worse approximation for the angular

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[1] F. G. Allen and G. W. Gobeli, Phys. Rev. **144**, 558 (1966); M. L. Cohen and J. C. Phillips, *ibid.* **139**, A912 (1965); D. Brust, M. L. Cohen, and J. C. Phillips, Phys. Rev. Letters **9**, 389 (1962); W. E. Spicer and R. E. Simon, *ibid.* **9**, 389 (1962).

[2] C. N. Berglund and W. E. Spicer, Phys. Rev. **136**, A1044 (1964); D. Brust, *ibid.* **139**, A489 (1965).

[3] G. W. Gobeli, F. G. Allen, and E. O. Kane, Phys. Rev. Letters **12**, 94 (1964); E. O. Kane, *ibid.* **12**, 97 (1964).

[4] G. A. Baraff, Phys. Rev. **135**, A528 (1964).