One- and Two-Photon Transitions of Atoms in Solids*

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The theory of one- and two-photon transitions between a given pair of impurity levels of the same parity is developed. As is well known, lattice vibrations assist the otherwise forbidden one-photon transition, increasing its intensity with temperature. The two-photon transition rate is shown to have a complementary decrease with increasing temperature. A measurement of both temperature dependences determines the effective frequency and coupling constant for the interaction. The formalism is applied to predicting the two-photon transition rate for the $4d^{10}$-$4d^{9}5s$ transition of the silver ion in NaCl:Ag. For an experiment using a ruby laser and an ultraviolet beam the maximum absorption coefficient predicted for the ultraviolet beam is $3.2 \times 10^{-48} FN$ cm^{-1} at low temperatures, where F is the flux (photons/cm^2 sec) of the laser and N is the Ag$^+$ concentration. This should be within reach of present experimental techniques.

I. INTRODUCTION

THE well-known theory of the simultaneous absorption of two photons by an atom[1] has been extended to impurity atoms in a solid by Kleinman.[2] He estimated transition rates by assuming that only a single intermediate state is of importance and that the one-photon oscillator strengths connecting it to both initial and final states are unity. Other two-photon calculations have been made for band-to-band transitions[3] and excitons.[4] Experimental observations of various two-photon absorption processes have also been reported.[5]

In static systems possessing inversion symmetry, two-photon dipole transitions may take place only between states of the same parity. Transitions between such pairs are dipole-forbidden in ordinary single-photon spectroscopy. In a crystal (or molecule), however, interaction with vibrations may admix a small amount of states of opposite parity giving rise to a one-photon transition rate which increases with temperature. A now familiar example of these vibrationally assisted transitions is afforded by absorption from the d^{10} ground state to the (mostly) d^9s configuration of a silver ion included as a substitutional impurity in an alkali halide lattice. These temperature-dependent absorption bands have been investigated in NaCl:Ag by Martienssen.[6] This work has recently been extended over a wider spectral range and to other alkali halides

by Onaka et al.[7] and by Fussganger.[8] Theoretical interpretations of these spectra have been made by Knox[9] and by Conway et al.[10]

In this paper we point out that one may advantageously study one- and two-photon transitions to the same state, at least in systems displaying vibrationally assisted spectra. We demonstrate that the one- and two-photon spectra have strikingly different temperature dependence, the strength of the two-photon transition falling off as increasing temperature mixes in more of an odd-parity excited state. It is found that comparison of these one- and two-photon spectra allows simultaneous determination of the effective frequency and coupling constant of the interacting lattice modes independent of a knowledge of concentration.

We address ourselves to the particular example of NaCl:Ag. In this case it is possible to make a quite careful evaluation of the two-photon matrix element. For the model adopted the technique of "averaging" energy denominators is not only equivalent to a time-dependent variational treatment, but also produces an approximate upper bound for the transition rate. We also calculate the contribution of the radiation Hamiltonian's term in A^2 which couples opposite parity states. This interaction will cause transitions between the ground state and the vibrationally admixed odd-parity part of the final state. It is found to be negligible.

The model for the calculation is presented in Sec. II. The theory for one and two photon transitions to the same state is presented in Sec. III where the two-photon results are cast into a form suitable for the application to NaCl:Ag given in Sec. IV. The calculation is briefly discussed in Sec. V. Detailed evaluation of matrix elements, and the polarization dependence of two-photon processes are given in the Appendix.

[1] M. Goeppert-Mayer, Ann. Physik 9, 273 (1931).
[2] D. A. Kleinman, Phys. Rev. 125, 87 (1962).
[3] R. Braunstein, Phys. Rev. 125, 475 (1962).
[4] R. Loudon, Proc. Phys. Soc. (London) 80, 952 (1962).
[5] W. L. Peticolas, J. P. Goldsborough, and K. E. Rieckhoff, Phys. Rev. Letters 10, 43 (1963); S. Singh and B. P. Stoicheff, J. Phys. Chem. 38, 2032 (1963); W. Kaiser and C. G. B. Garrett, Phys. Rev. Letters 7, 229 (1961); J. J. Hopfield and J. M. Worlock, Phys. Rev. 137, A1455 (1965).
[6] W. Martienssen, *Proceedings of the International Conference on Semiconductor Physics* (Czechoslovakia Academy of Science, Prague, 1960), p. 760.

[7] R. Onaka, A. Fukuda, K. Inohara, T. Mabuchi, and Y. Fujioka (to be published).
[8] K. Fussganger, Diplomarbeit, Johann Wolfgang Goethe Universitat, Frankfurt am Main, 1964 (to be published).
[9] R. S. Knox, J. Phys. Soc. Japan Suppl. 18, 268 (1963).
[10] J. Conway, D. Greenwood, J. Krumhansl, and W. Martienssen, J. Phys. Chem. Solids 24, 239 (1963).

II. THE MODEL

The electronic levels of our model system, chosen to idealize NaCl:Ag, are shown in Fig. 1. These specify the states of the system with the lattice at its static equilibrium. The ground state ψ_g is taken to be spherically symmetric (the $4d^{10}$ configuration of Ag^+ in NaCl:Ag). The lowest excited state ψ_s is of even parity (in NaCl:Ag it is built from the $4d^95s$ configuration). Above this lies the odd parity state $\psi_p(4d^95p)$ followed by a continuum of conduction-band states. Here and hereafter we shall neglect the crystal-field splittings of the excited states, the resulting integrated absorption coefficient being the area under all bands.

We assume that an electron-phonon interaction linear in an odd-parity lattice mode mixes ψ_s and ψ_p, giving rise to phonon-assisted transitions. Mixing of ψ_s with other excited states, and perturbations of the ground state are neglected. We work in terms of a single "effective" mode; generalization to many modes is straightforward. The ground state is represented by the Hartree-Fock wave function for the free ion. The excited-state wave functions are approximated by Slater-type orbitals orthogonalized to the ion core. Overlap of the wave functions with those on neighboring ions is neglected. In two-photon processes we consider two light beams each of whose photon energy is smaller than $E_s - E_g$.

III. THEORY

In the lattice, phonon coupling gives a perturbed excited-state wave function

$$\psi_f = c_s\psi_s + c_p\psi_p; \quad |c_s|^2 + |c_p|^2 = 1 \tag{1}$$

for the final state of interest. For a linear electron-lattice interaction H_{eL}, the mixing can be described in terms of a coupling constant γ,

$$c_p = \langle \psi_p | H_{\text{eL}} | \psi_s \rangle / (E_s - E_p) = \gamma Q, \tag{2}$$

where Q is the normal coordinate[11] for the mode in question and E_s and E_p are the eigenvalues of ψ_s and ψ_p in the static lattice. In terms of the coupling constant and the phonon frequency ω_{ph}, the integrated absorption coefficient for the one-photon (phonon-assisted) transition between ψ_g and ψ_f is well known to be[12]

$$K = \int \mu(E)dE = \left(\frac{\mathscr{E}_{\text{loc}}}{\mathscr{E}_0}\right)^2 \frac{N}{n} (2\pi)^2 \frac{e^2}{\hbar c}$$

$$\times E_{fg} |\langle \psi_p | \boldsymbol{\varepsilon} \cdot \mathbf{r} | \psi_g \rangle|^2 \gamma^2 \langle Q^2 \rangle_T. \tag{3a}$$

In (3a) $(\mathscr{E}_{\text{loc}}/\mathscr{E}_0)$ is the effective field ratio, N the concentration of impurities, and n the (slowly varying)

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[11] We adopt the convention of Born and Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, 1956) and absorb the square root of the "mass" of the mode into the coordinate.

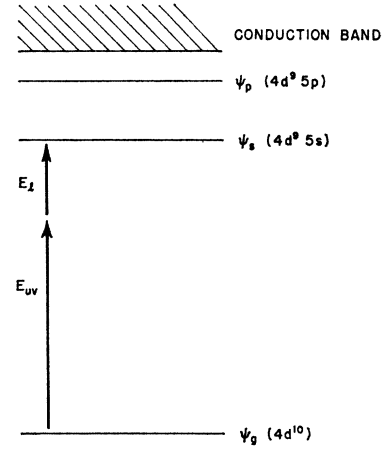[12] R. Kubo and Y. Toyozawa, Progr. Theoret. Phys. (Kyoto) **13**, 160 (1955).

FIG. 1. Model for the electronic states of an impurity atom in the rigid lattice.

index of refraction of the pure host material at the mean energy of the absorption E_{fg}. The (unit) polarization vector of the incident light is $\boldsymbol{\varepsilon}$. $\langle Q^2 \rangle_T$ indicates a thermal average of Q^2 at temperature T and enters via the appearance of $\gamma Q\psi_p$ in the matrix element for the transition; otherwise (3a) is just the ordinary "generalized Smakula equation" for the absorption by an impurity in a solid.[13] Performing the indicated thermal average[14] gives

$$K = \left(\frac{\mathscr{E}_{\text{loc}}}{\mathscr{E}_0}\right)^2 \frac{N}{n} (2\pi)^2 \frac{e^2}{\hbar c} E_{fg} |\langle \psi_p | \boldsymbol{\varepsilon} \cdot \mathbf{r} | \psi_g \rangle|^2$$

$$\times \frac{\gamma^2\hbar}{2\omega_{\text{ph}}} \coth\frac{\hbar\omega_{\text{ph}}}{2kT}. \tag{3b}$$

In the dipole approximation, the rate $w_{fg}^{(2)}$ of simultaneous absorption of two photons one of energy E_{uv} and the other E_l by an atom is given by[1]

$$w_{fg}^{(2)} = (2\pi)^3 \left(\frac{e^2}{\hbar c}\right)^2 E_l E_{\text{uv}} F_l F_{\text{uv}}$$

$$\times \left| \sum_n \frac{\langle f | \boldsymbol{\varepsilon}_{\text{uv}} \cdot \mathbf{r} | n \rangle \langle n | \boldsymbol{\varepsilon}_l \cdot \mathbf{r} | g \rangle}{E_{ng} - E_l} \right.$$

$$\left. + \frac{\langle f | \boldsymbol{\varepsilon}_l \cdot \mathbf{r} | n \rangle \langle n | \boldsymbol{\varepsilon}_{\text{uv}} \cdot \mathbf{r} | g \rangle}{E_{ng} - E_{\text{uv}}} \right|^2. \tag{4}$$

The second-order transition takes place from initial state g to final state f through coupling with intermediate states n. F_l and F_{uv} are the fluxes (photons $\text{cm}^{-2} \text{ sec}^{-1}$) of the two beams which have polarization vectors $\boldsymbol{\varepsilon}_l$ and $\boldsymbol{\varepsilon}_{\text{uv}}$. E_{ng} is the energy of the intermediate state relative to the ground state, conservation of energy

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[13] See, for example, D. L. Dexter, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. VI.

[14] See Ref. 11, Chap. IV, Sec. 16.

demands that $E_{fg}=E_{uv}+E_l$ and we assume that neither beam is capable of causing transitions by itself (cf., Fig. 1).

One may define an effective absorption coefficient $\mu_{uv}(E)$, as the energy removed from the "ultraviolet" beam per unit time for a beam of unit intensity in the presence of the "laser" beam. It is then a straightforward matter to obtain the integrated absorption coefficient for a concentration of N impurities dispersed in a dielectric medium having indices of refraction n_l and n_{uv} at energies E_l and E_{uv}. This gives one a "two-photon Smakula equation" of the form

$$K_{uv}=\int \mu_{uv}(E)dE=\left(\frac{\mathcal{E}_{loc,l}\mathcal{E}_{loc,uv}}{\mathcal{E}_{0,l}\mathcal{E}_{0,uv}}\right)^2 (2\pi)^3\frac{e^4}{\hbar c}\frac{E_l\bar{E}_{uv}}{n_l n_{uv}}F_l N$$
$$\times |R_{fg}^{(2)}|^2(1-\gamma^2\langle Q^2\rangle_T). \quad (5)$$

In writing (5) we have assumed that the energy of the transition is large compared to the width of the absorption band; $\bar{E}_{uv}$ is the average energy of the ultraviolet radiation over the absorption band. $R_{fg}^{(2)}$ is the "second-order matrix element"

$$R_{fg}^{(2)}=\sum_n\left(\frac{\langle\psi_s|\mathbf{\epsilon}_{uv}\cdot\mathbf{r}|\psi_n\rangle\langle\psi_n|\mathbf{\epsilon}_l\cdot\mathbf{r}|\psi_g\rangle}{E_{ng}-E_l}\right.$$
$$\left.+\frac{\langle\psi_s|\mathbf{\epsilon}_l\cdot\mathbf{r}|\psi_n\rangle\langle\psi_n|\mathbf{\epsilon}_{uv}\cdot\mathbf{r}|\psi_g\rangle}{E_{ng}-\bar{E}_{uv}}\right). \quad (6)$$

The $\mathcal{E}$'s are the various effective fields of laser and ultraviolet frequency. The final thermal factor in parentheses in (5) arises from the lowest order approximation to c_s appearing in (1) as demanded by normalization and the form (2) of c_p. We may rewrite (5) as

$$K_{uv}=\left(\frac{\mathcal{E}_{loc,l}\mathcal{E}_{loc,uv}}{\mathcal{E}_{0,l}\mathcal{E}_{0,uv}}\right)^2(2\pi)^3\frac{e^4}{\hbar c^2}\frac{E_l\bar{E}_{uv}}{n_l n_{uv}}F_l N|R_{fg}^{(2)}|^2$$
$$\times\left(1-\frac{\gamma^2\hbar}{2\omega_{ph}}\coth\frac{\hbar\omega_{ph}}{2kT}\right). \quad (7)$$

This distinctive temperature dependence of the two-photon absorption coefficient can be viewed as the complement of the phonon assistance of the one-photon transition between the same pair of levels. As ψ_p is mixed into ψ_f by the lattice some ψ_s is "mixed out," resulting in a decrease in the two-photon intensity. This temperature dependence should be most useful in the positive identification of two-photon absorption processes resulting from dipolar terms in the radiation Hamiltonian. As we shall see, two-photon transitions between states of opposite parity arising from higher moments of the term in $\mathbf{A}\cdot\mathbf{A}$ behave quite differently.

If we wish to compute a transition rate or absorption coefficient we must make simplifying approximations

in the second-order matrix element $R_{fg}^{(2)}$. An obvious simplification is the analog of the one customarily used in the theory of dispersion forces.[15] We take an "average" energy denominator independent of state, move it outside the sum and then evaluate what remains by using the closure property. If $\bar{E}$ is the average so defined, we obtain

$$|R_{fg}^{(2)}|^2=\left|\left(\frac{1}{\bar{E}-E_l}+\frac{1}{\bar{E}-\bar{E}_{uv}}\right)\right.$$
$$\left.\times\langle\psi_s|(\mathbf{\epsilon}_{uv}\cdot\mathbf{r})(\mathbf{\epsilon}_l\cdot\mathbf{r})|\psi_g\rangle\right|^2. \quad (8)$$

For a spectrum of the type shown in Fig. 1 it is obvious that an upper bound to the transition rate is obtained by setting $\bar{E}=E_{pg}$, since ψ_p gives the smallest energy denominator of any possible intermediate state appearing in (6). More generally, Yaris[16] has shown that the denominator "averaging" process corresponds to a variational treatment of the time-dependent Schrödinger equation. A similar technique has been employed by Axe[17] in considering two-photon and Raman processes on rare-earth ions and by Gold and Bebb[18] in considering multiphoton ionization.

Recently Ianuzzi and Polacco[19] have emphasized that the term $(e^2/2mc^2)\mathbf{A}\cdot\mathbf{A}$ in the perturbation Hamiltonian can, going beyond the dipole approximation, cause two-photon transitions between states of opposite parity. Since this process may contribute to the over-all two-photon rate in the present problem, via coupling to ψ_p, we sketch the first-order perturbation theory for the interaction. For two beams of different frequencies ω_{uv} and ω_l, the relevant part of the Hamiltonian is

$$H_{A^2}'=(e^2/mc^2)\mathbf{A}_l\cdot\mathbf{A}_{uv}$$
$$\times\exp i[(\mathbf{k}_l+\mathbf{k}_{uv})\cdot\mathbf{r}-(\omega_l+\omega_{uv})t], \quad (9)$$

where the $\mathbf{k}$'s are wave vectors.

Retaining only the lowest nonvanishing multipole term, the atomic transition rate for this perturbation is

$$w_{A^2}=[(2\pi)^3e^4/m^2c^2](F_lF_{uv}/\omega_l\omega_{uv})$$
$$\times|(\mathbf{\epsilon}_l\cdot\mathbf{\epsilon}_{uv})\langle f|(\mathbf{k}_l+\mathbf{k}_{uv})\cdot\mathbf{r}|g\rangle|^2. \quad (10)$$

This vanishes identically for perpendicularly polarized beams and so, in any event, may be eliminated experimentally and subsequently measured independently. It should also be noted that this result gives a vanishing rate for a single-beam two-photon experiment performed with circularly polarized light.

If we again define an effective absorption coefficient

[15] See, for example, the review by H. Margenau, Rev. Mod. Phys. **11**, 1 (1939).
[16] R. Yaris, J. Chem. Phys. **39**, 2474 (1963).
[17] J. D. Axe, Phys. Rev. **136**, A42 (1964).
[18] A. Gold and H. B. Bebb, Phys. Rev. Letters **14**, 60 (1965).
[19] M. Ianuzzi and E. Polacco, Phys. Rev. Letters **13**, 371 (1964).

$\mu_{uv}(E; A^2)$ and integrate, we obtain

$$K_{uv}(A^2) = \int \mu_{uv}(E; A^2) dE$$

$$= \left(\frac{\mathscr{E}_{loc,uv}\mathscr{E}_{loc,l}}{\mathscr{E}_{0,uv}\mathscr{E}_{0,l}}\right)^2 \frac{(2\pi)^3 e^4 \hbar F_l N}{m^2 c^4 n_l n_{uv}} |\varepsilon_l \cdot \varepsilon_{uv}|^2$$

$$\times (n_l^2(E_l/\bar{E}_{uv}) + n_{uv}^2(\bar{E}_{uv}/E_l) + 2n_l n_{uv} \hat{k}_l \cdot \hat{k}_{uv})$$

$$\times |\langle \psi_p | x | \psi_g \rangle|^2 \frac{\gamma^2 \hbar}{2\omega_{ph}} \coth\frac{\hbar\omega_{ph}}{2kT}. \quad (11)$$

The $\hat{k}$'s are unit vectors in the directions of beam propagation.

IV. APPLICATION TO NaCl:Ag

The matrix element in (8) may be rewritten as

$$|\langle \psi_s | (\varepsilon_l \cdot \mathbf{r})(\varepsilon_{uv} \cdot \mathbf{r}) | \psi_g \rangle|^2 = |M_{sd}|^2 C(\varepsilon_l, \varepsilon_{uv}), \quad (12)$$

where

$$M_{sd} = \int f_{5s} r^2 f_{4d} dr,$$

is the radial part of the matrix element of r^2 between the 4d and 5s orbitals for Ag$^+$, and the f's are the usual radial wave functions. This has been evaluated using the Hartree-Fock function[20] for the ground state (4d) and Slater-type functions[21] for the excited state. The details of this evaluation (showing a remarkable insensitivity of result to choice of parameters) are treated in the Appendix. $C(\varepsilon_l, \varepsilon_{uv})$ is a factor arising from the angular integration and averaging. It is discussed in detail in the Appendix where its value for various states of beam polarization is tabulated. Typically it is about 0.15.

The Lorentz-Lorenz form has been used throughout for the effective field corrections, i.e.,

$$(\mathscr{E}_{loc,uv}\mathscr{E}_{loc,l}/\mathscr{E}_{0,uv}\mathscr{E}_{0,l})^2 = \{[(n_l^2+2)/3][(n_{uv}^2+2)/3]\}^2,$$

appears in the two-photon absorption coefficient. We take $E_l = 1.78$ eV appropriate to the ruby laser and $\bar{E}_{uv} = 5.02$ eV for the (weighted) peak position as given by the data of Onaka et al.[7] $\bar{E}$ is (conservatively) taken as the band gap 7.8 eV and the indices are $n_l = 1.54$ and $n_{uv} = 1.65$. From the Appendix M_{sd} is typically $2.5a_0^2$. These parameters give

$$K_{uv} = 1.53 \times 10^{-48} C(\varepsilon_l, \varepsilon_{uv})$$
$$\times NF_l(1 - (\gamma^2 \hbar/2\omega_{ph})\coth(\hbar\omega_{ph}/2kT))$$
$$\times (\text{eV cm}^{-1}). \quad (13)$$

Taking $C = 0.15$ and assuming a Gaussian band of

[20] B. H. Worsley, Proc. Roy. Soc. (London) **A247**, 390 (1958).
[21] J. C. Slater, Phys. Rev. **36**, 57 (1930).

width 0.1 eV we obtain a peak absorption coefficient

$$\mu_{uv,max} = 3.2 \times 10^{-48} NF_l \ (\text{cm}^{-1})$$

at 0°K. For typical concentrations of $N = 10^{19}$ cm^{-3}, one has an easily measured absorption coefficient of 1 cm^{-1} for a laser flux of 4×10^{28} photons cm^{-2} sec^{-1}. Thus, the measurement seems practical, since fluxes greater than 10^{30} can be obtained. Unfortunately, very high power laser beams are capable of doing gross macroscopic damage to transparent crystals, probably making it necessary to perform measurements at lower power and giving rise to considerable additional difficulty.

The A^2 term may be similarly evaluated. The radial matrix element entering is

$$M_{pd} = \int f_{5p} r f_{4d} dr = 1.0 a_0$$

as discussed in the Appendix. The integrated absorption coefficient is

$$K_{uv}(A^2) = 7.43 \times 10^{-55}$$
$$\times (8.52 + 5.08|\hat{k}_l \cdot \hat{k}_{uv}|)B(\varepsilon_l, \varepsilon_{uv})NF_l$$
$$\times (\gamma^2 \hbar/2\omega_{ph})\coth(\hbar\omega_{ph}/2kT) \ (\text{eV cm}^{-1}). \quad (14)$$

$B(\varepsilon_l, \varepsilon_{uv})$ is an angular factor which varies between zero and $\frac{4}{3}$ and is tabulated in the Appendix. Even for the largest values of B, $K_{uv}(A^2)$ will be six orders of magnitude smaller than the dipole absorption given at low temperatures by (13) and almost surely unobservable under presently attainable experimental conditions. This situation will not change substantially at higher temperatures.

The temperature dependence of one-photon absorption is shown and fit in Fig. 2. We use the results of Ref. 7 which reveal that the dominant temperature-dependent transition lies at 6.9 eV, an energy above the range accessible to Martienssen's instrument.[6] It gives a one-photon oscillator strength an order of magnitude
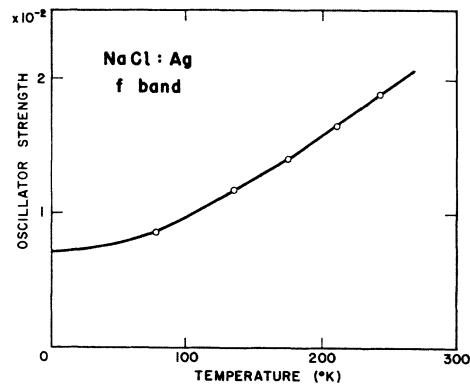

FIG. 2. Fit of the temperature-dependence data of Onaka et al. (Ref. 7). Over 90% of the total oscillator strength comes from the "f" (6.9-eV) band shown here. The fitted solid curve drawn through the experimental points is of the form $f(T) = f(0) \times \coth(\hbar\omega_{ph}/2kT)$ with $\omega_{ph} = 2.5 \times 10^{13}$ sec^{-1}.
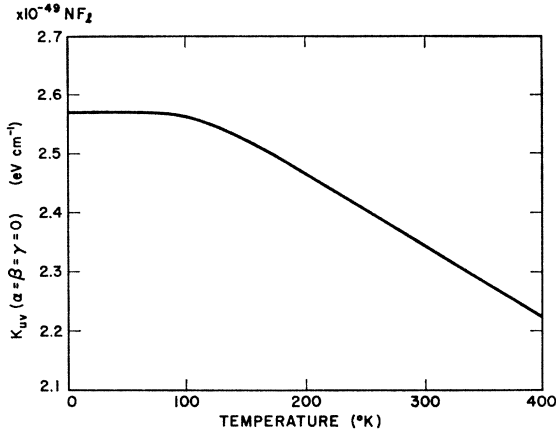
FIG. 3. Temperature dependence of the integrated two-photon absorption coefficient for NaCl:Ag$^+$. The beams are polarized parallel to each other. Using values obtained from Fig. 2 and matrix elements given in the text, K_{uv} is given by $K_{uv} = 2.72 \times 10^{-49} N F_l [1 - 0.044 \coth(\hbar\omega_{ph}/2kT)]$, where $\omega_{ph} = 2.5 \times 10^{-13}$ sec^{-1}.

greater than that previously quoted. The fit to the data gives $\omega_{ph} = 2.5 \times 10^{13}$ sec^{-1}. Inserting the value of the $4d-5p$ dipole-matrix element given above we find

$$(\gamma^2 \hbar / 2\omega_{ph}) = 4.4 \times 10^{-2}.$$

Figure 3 uses the parameters thus obtained and the above value of the coupling constant to plot the predicted temperature dependence for two-photon transitions in NaCl:Ag as given by Eq. (13). In practice it is hoped that this procedure can be reversed, measurements of the two temperature-dependent spectra being used to determine γ and ω_{ph}.

Comparison of the present results with the rough estimates of Kleinman[2] is best done via his Eq. (6). It gives an integrated absorption coefficient of 1.09 $\times 10^{-48} N F_l$ eV cm^{-1}. Presumably this should be interpreted as already containing the appropriate angular factors. Taking the maximum value of the angular factor $C(\varepsilon_l, \varepsilon_{uv}) = 0.178$, Eq. (13) gives $2.7 \times 10^{-49} N F_l$ eV cm^{-1}. Hence, the maximum absorption strength predicted here is one fourth that estimated by Kleinman's approximation. Even this close an agreement is likely fortuitous.

V. DISCUSSION

A simple method for obtaining two-photon absorption coefficients a priori has been presented. The approximation of taking an "average" energy denominator provides one with a reasonable estimate (or even an upper bound) for the rate. It has been shown that the strength of a two-photon dipole absorption has a unique and readily identified temperature dependence arising from the same phonon interaction which assists the otherwise forbidden single-photon transition between the same pair of levels. Simultaneous measurement of one- and two-photon absorption allows independent

measurement of the effective phonon frequency and coupling constant.

The A^2 coupling has been examined and its angular and temperature dependence explicitly noted. For NaCl:Ag it gives a negligible contribution to the two-photon absorption.

The predicted peak two-photon absorption coefficient of $\sim 3 \times 10^{-48} F_l N$ cm^{-1} at low temperatures should be measurable with current experimental techniques, even though care will be necessary in avoiding macroscopic damage to the samples by the intense laser beam.

The neglect of crystal-field splittings is not a serious limitation on the applicability of the present work. Inoue and Toyozawa have recently given selection rules for two photon transitions between crystal field split levels.[22] These should prove of great use in making explicit symmetry assignments to the various peaks observed in the spectrum of NaCl:Ag.

Finally it should be remarked that the neglect of overlap corrections and the use of Slater-type wave functions in evaluating the transition matrix elements are not expected to cause gross errors. It has been found previously that overlap corrections to dipole-matrix elements are extremely small.[23] The insensitivity of the matrix elements to the choice of parameters in the Slater functions gives one confidence that the results are not artifacts of that particular approximation.

ACKNOWLEDGMENTS

APPENDIX

The radial-matrix elements M_{sd} and M_{pd} have been evaluated for the silver ion using the Hartree-Fock function for the $4d$ shell[20] and Slater-type functions for the $5s$ and $5p$ orbitals. These are of the (unnormalized)

TABLE I. The radial integrals $M_{sd} = \int f_{5s} r^2 f_{4d} dr$ and $M_{pd} = \int f_{5p} r f_{4d} dr$ as a function of the parameter $Z-S$. Lengths are expressed in units of a_0 and $n^* = 4$ is used throughout.

$(Z-S)/n^*$	M_{sd}	M_{pd}
1.7	2.67	0.97
1.8	2.67	0.99
1.9	2.70	1.00
2.0	2.67	1.01
2.1	2.65	1.02
2.2	2.59	1.01
2.3	2.51	0.99
2.4	2.51	1.00
2.5	2.45	1.00
2.6	2.40	1.00
2.7	2.34	0.98

[22] M. Inoue and Y. Toyozawa, J. Phys. Soc. Japan 20, 363 (1965).
[23] See, for example, A. Gold, J. Phys. Chem. Solids 18, 218 (1961).

form

$$f_S(r) = r^{n*}e^{-(Z-S)/n*},\qquad\text{(A1)}$$

where $n*$ is the "effective" principal quantum number and $Z-S$ is taken as a parameter. These functions are orthogonalized to the inner electron wave functions and normalized prior to use. The results are given in Table I. A remarkable insensitivity to parameter choice should be noted. The peculiar "wiggles" in the value of M_{pd} are due to round error and of no particular interest. All numerical integrations were performed on the University of Rochester Computing Center's IBM 7074 using programs by T. H. Keil.[24]

The angular factor $C(\varepsilon_1,\varepsilon_2)$ appearing in the matrix element (12) is

$$C(\varepsilon_1,\varepsilon_2) = Av_{\epsilon_1,\epsilon_2}2\sum_m\left|\int Y_2{}^m Y_0{}^0\frac{(\varepsilon_1\cdot r)(\varepsilon_2\cdot r)}{r^2}d\Omega\right|^2,\quad\text{(A2)}$$

where the average over polarizations is to be taken when one or both beams are unpolarized. Defining angles α, β, and γ as in Fig. 4 and its caption one obtains the following expressions for C.

(a) Both Beams Unpolarized

$$C(\varepsilon_1,\varepsilon_2) = \frac{1}{5\cdot3^2\cdot2}\frac{14+13\tan^2\alpha}{1+\tan^2\alpha}.\qquad\text{(A3)}$$

(b) Beam 1 Polarized, Beam 2 Unpolarized

$$C = (1/5\cdot3^2)[7+(6+\sin^2\beta)\tan^2\alpha]/[1+\tan^2\alpha].\quad\text{(A4)}$$

(c) Both Beams Polarized

$$C = (2/5\cdot3^2)[(3+\cos^2\alpha)\cos^2\beta\cos^2\gamma$$
$$+3\sin^2\beta\cos^2\gamma+3\cos^2\beta\sin^2\gamma+4\sin^2\beta\sin^2\gamma$$
$$+2\cos\alpha\sin\beta\sin\gamma\cos\gamma].\quad\text{(A5)}$$
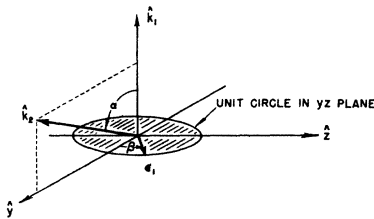
FIG. 4. Angles appearing in $C(\varepsilon_1,\varepsilon_2)$ and $B(\varepsilon_1,\varepsilon_2)$ $\cos\alpha = \hat{k}_1\cdot\hat{k}_2$; $\cos\beta = \varepsilon_1\cdot\hat{y}$; $\cos\gamma = \varepsilon_2\cdot(\hat{z}\times\hat{k}_2)$. The unit vector $\hat{k}_1$ is taken as the x direction, placing ε_1 in the y-z plane. The angle between ε_1 and $\hat{y}$ is β. The angle between the directions of the two beams is α. γ is the angle between ε_2 and the projection of y on the plane perpendicular to $\hat{k}_2$.

[24] T. H. Keil, University of Rochester, 1964 (unpublished).

TABLE II. $C(\varepsilon_1,\varepsilon_2)$ and $B(\varepsilon_1,\varepsilon_2)$ at various beam and polarization angles. See Fig. 4 and its caption for definitions of angles. The first column refers to the three cases of beam polarization: (a) both unpolarized; (b) beam 1 polarized; (c) both beams polarized.

Case	α	β	γ	$C(\varepsilon_1,\varepsilon_2)$	$B(\varepsilon_1,\varepsilon_2)$
	0	...	...	0.156	0.667
a.	$\pi/4$	...	...	0.150	0.500
	$\pi/2$	...	...	0.144	0.333
	0	any	...	0.156	0.667
	$\pi/4$	0	...	0.144	0.333
	$\pi/4$	$\pi/4$	...	0.150	0.500
b.	$\pi/4$	$\pi/2$	...	0.156	0.667
	$\pi/2$	0	...	0.133	0
	$\pi/2$	$\pi/4$	...	0.144	0.333
	$\pi/2$	$\pi/2$	...	0.156	0.667
	0	0	0	0.178	1.333
	0	0	$\pi/4$	0.155	0.667
	0	0	$\pi/2$	0.133	0
	0	$\pi/4$	$\pi/4$	0.178	1.333
	0	$\pi/4$	$\pi/2$	0.155	0.667
	0	$\pi/2$	$\pi/2$	0.178	1.333
c.	$\pi/4$	0	0	0.155	0.667
	$\pi/4$	0	$\pi/4$	0.144	0.333
	$\pi/4$	0	$\pi/2$	0.133	0
	$\pi/4$	$\pi/4$	$\pi/4$	0.166	0.972
	$\pi/4$	$\pi/4$	$\pi/2$	0.155	0.667
	$\pi/4$	$\pi/2$	$\pi/2$	0.178	1.333
	$\pi/2$	0	any	0.133	0
	$\pi/2$	$\pi/4$	$\pi/4$	0.144	0.333
	$\pi/2$	$\pi/4$	$\pi/2$	0.155	0.667
	$\pi/2$	$\pi/2$	$\pi/2$	0.178	1.333

These results are tabulated in Table II. Similarly the factor B appearing in (14) is

$$B(\varepsilon_1,\varepsilon_2) = \sum_{m_1}\sum_{m_2}\left|\int Y_2{}^{m_2}Y_1{}^{m_1}\frac{k_1+k_2}{|k_1+k_2|}\cdot\frac{r}{r}d\Omega\right|^2$$
$$\times Av_{\epsilon_1,\epsilon_2}|\varepsilon_1\cdot\varepsilon_2|^2.\quad\text{(A6)}$$

Evaluation gives:

(a) Both Beams Unpolarized

$$B = \tfrac{1}{3}(2+\tan^2\alpha)/(1+\tan^2\alpha).\qquad\text{(A7)}$$

(b) Beam 1 Polarized, Beam 2 Unpolarized

$$B = \tfrac{2}{3}(1+\sin^2\beta\tan^2\alpha)/(1+\tan^2\alpha).\qquad\text{(A8)}$$

(c) Both Beams Polarized

$$B = \tfrac{4}{3}(\cos\alpha\cos\beta\cos\gamma+\sin\beta\sin\gamma)^2.\qquad\text{(A8)}$$

Values are tabulated in Table II.