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Two-Photon Excitation of Electrons in Solids

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Excitations of electrons in solids in the presence of two electromagnetic beams are discussed. Two excitation processes are considered: (a) transition of an electron from valence band 1 to conduction band 2, absorbing a photon with energy $\hbar\omega$, and subsequent excitation of the electron to conduction band 3 absorbing a photon with energy $\hbar\Omega$; (b) excitation of an electron to band 2, followed by an intraband transition accompanied by the emission of a phonon, and subsequent absorption of a photon $\hbar\Omega$ and excitation of the electron to band 3. It is shown that there is a distinct threshold energy for the process of type (a) and in certain cases there is a distinct threshold energy for processes of type (b). The transition rate is evaluated as a function of $\hbar\omega$ for values close to the threshold value. At threshold, cascade two-photon transition may be allowed in points, along a line, or over a surface in $\vec{K}$ space. These different conditions lead to different types of transition-rate spectra. The effect of the intensity of the Ω beam on the different spectra is discussed. The intensity is allowed to exceed the values for which cascade transitions may be considered. The transition-rate spectrum for process (b) is also evaluated. It is shown that for polar crystals, process (b) will lead to transition rates of the same order of magnitude as those obtained in process (a). Possible use of these effects for the investigation of band structure of solids is discussed.

I. INTRODUCTION

The development of high-power lasers has opened the way to the investigation of nonlinear optical effects. However, the use of these effects as a spectroscopic tool has remained quite limited because high-power radiation could be obtained only in discrete frequencies. In cases where an ordinary light source could be used as one of the beams participating in the nonlinear process, nonlinear effects were, in fact, used as spectroscopic tools. For example, two-photon absorption processes have been used for the investigation of band structure in solids at critical points in the Brillouin zone.[1] Two-photon absorption has selection rules which differ from those of linear optical absorption, thus additional information can be obtained from these measurements.

Dye lasers[2] provide high-power beams with frequencies which can be varied continuously, thus opening new possibilities for the use of nonlinear optical phenomena as spectroscopic tools. In a recent paper, Yacoby[3] has shown that nonlinear optical spectroscopy may indeed provide information which could not be obtained by linear optical spectroscopy, namely, information about electronic band structure along lines of high symmetry in the Brillouin zone. Such an experiment consists of measuring the intensity of a beam with frequency equal to $\omega+\Omega$ produced by two beams with frequencies equal to ω and Ω as a function of ω. It has been shown that this intensity varies very significantly in the vicinity of the point in the crystal-momentum space at which the two surfaces F_{12}, defined by $\epsilon_{12}(\vec{K})=\hbar\omega$, and F_{23}, defined by $\epsilon_{23}(\vec{K})=\hbar\Omega$, just touch each other. [$\epsilon_{12}(\vec{K})$ and $\epsilon_{23}(\vec{K})$ are the energy differences between bands 2 and 1, and 3 and 2, respectively.] In most cases such points of contact will occur along lines of high symmetry. Therefore, spectroscopic measurements of this kind may provide information that can be directly compared with theory about electronic band structure along lines of high symmetry. This experiment has, however, two fundamental limitations: (i) It can be applied only to crystals which have no inversion symmetry; (ii) strong variation in the spectrum occurs, at the point where the two surfaces F_{12} and F_{23} touch, only if the gradients $\vec{\nabla}_{\vec{K}}\epsilon_{12}(\vec{K})$ and $\vec{\nabla}_{\vec{K}}\epsilon_{23}(\vec{K})$ at the points of contact are in opposite directions.

In this paper we shall discuss the transition rate of electrons from a valence band (band 1) to a conduction band (band 3) in the presence of two electromagnetic beams, as a function of the photon energy of one of these beams. We shall show that measurement of this transition rate may provide information about the band structure in cases where measurement of the intensity of a sum frequency beam fails. In addition, the rate of two-photon transitions assisted by the emission of optical phonons will be evaluated as a function of the photon energy of one of the incident beams. It will be shown that in certain cases such an effect has a distinct threshold and may be of the same order of magnitude as the two-photon transition rate.

The condition for a threshold for two-photon and for two-photon phonon-assisted transitions are discussed in Sec. II. In Sec. III we evaluate the nonlinear transition rate without phonon assistance, whereas in Sec. IV we evaluate the two-photon pho-

non-assisted transition rates. A summary of the results and a brief discussion of the experimental possibilities are given in Sec. V.

II. CONDITIONS FOR THRESHOLD IN TWO-PHOTON CASCADE TRANSITION RATE

In the presence of an electromagnetic beam with photon energy $\hbar\omega$, the electrons that make the transition from band 1 to band 2 are located on the surface F_{12}. Some of these electrons may make transitions from band 2 to 3 in the presence of another beam with photon energy $\hbar\Omega$. These are located in $\vec{K}$ space at points common to the surfaces F_{12} and F_{23}. It is evident that the photon energy $\hbar\omega$ which constitutes the border value between allowed and unallowed cascade transition, corresponds to the surface F_{12} which just touches F_{23}. Two cases are of particular interest.

(i) Surfaces F_{12} and F_{23} are spheres. In this case the surfaces will coincide for certain photon energies giving rise to a very strong transition rate. Spherical surfaces will appear, for example, close to the Γ point in crystals with full cubic symmetry.

(ii) Surfaces F_{12} and F_{23} touch along a line. This case occurs when the surfaces are elipsoids or hyperboloids of revolution with a common axis. Such surfaces will be found, for example, near $\vec{K}=0$ in tetragonal crystals or in certain cases in cubic crystals near triply degenerate bands.

Electrons can be excited to band 3 in still another way. An electron on surface F_{12} makes a transition from band 1 to band 2 absorbing one photon $\hbar\omega$. Then the electron emits or absorbs one or more phonons thereby making intraband transitions. Electrons that arrive by means of these transitions at surface F_{23} may absorb an additional photon $\hbar\Omega$ and be excited to band 3. We shall denote such a process as two-photon phonon-assisted transition (TPPAT).

Let us now discuss the conditions for a threshold for such a process. We shall confine our discussion to phonon emission processes which are the dominant processes at low temperatures. $\hbar\omega_0$ is called the threshold photon energy if it is a border energy that separates values for which the TPPAT are allowed and forbidden. One readily observes that $\hbar\omega_0$ is a threshold energy for a given value $\hbar\Omega$ if the corresponding surfaces F_{12} and F_{23} satisfy the following condition:

$$\epsilon_2(\vec{K}) - \epsilon_2(\vec{K}') \leq \epsilon_{\vec{q}}\,, \tag{1}$$

where $\vec{K}$ is any point on F_{12}; $\vec{K}'$ is any point on F_{23}; $\epsilon_{\vec{q}}$ is the phonon energy with wave vector $\vec{q}$, and

$$\vec{q} = \vec{K} - \vec{K}'\,. \tag{2}$$

It is necessary that there be at least one point $\vec{K}$ and one point $\vec{K}'$ for which the equality holds.

Since the phonon energy $\epsilon_{\vec{q}}$ is very small compared to characteristic electronic energies, one may neglect it in the discussion of the relative position of the surfaces around threshold. Within this approximation the electron emitting a phonon will be found on a surface of constant energy in band 2 denoted by F_2. The condition for threshold stated above then requires that at threshold there should be at least one surface F_2 simultaneously tangent to both F_{12} and F_{23} and there should be no surface F_2 that cuts both of them. Note, however, that these are not sufficient conditions for the threshold.

We shall consider two cases.

Case a. Surfaces F_{12}, F_{23}, and F_2 have a common point of contact. In most cases the common point of contact will be located along lines of high symmetry in $\vec{K}$ space. One observes that condition (1) requires that F_2 be located between F_{12} and F_{23}. The threshold energy for this process is very close to the threshold energy of two-photon transitions. In fact, the difference between the photon energies corresponding to the two thresholds is of the order of $\epsilon_{\vec{q}}$. At first glance it appears that the TPPAT rate will be very much smaller than the two-photon transition rate. This is because the valence electrons that may make a transition to band 3 should be located on surface F_{12} close to the point of contact between F_{12} and F_2. After emitting a phonon, they are located somewhere on surface F_2, thus only a very small portion of them will be on surface F_{23}. There is, however, one type of electron-phonon interaction for which the electrons have a larger probability to arrive at F_{23}: This occurs in polar crystals in which the polar-phonon–electron interaction is dominant. The electron–polar-phonon interaction[4] is proportional to $|\vec{q}|^{-1}$, and since in this case there are points $\vec{K}$ and $\vec{K}'$ for which $|\vec{q}|$ is very small, the probability of the electrons arriving at F_{23} is large. In Sec. IV we shall show that in crystals with electron–polar-phonon interaction, the TPPAT around threshold is of the same order of magnitude as the two-photon transition rate.

Case b. Surface F_2 touches F_{12} and F_{23} in separate points in $\vec{K}$ space. In this case the TPPAT will be much smaller than the previously discussed rates. However, since this effect may precede the two-photon transition threshold, it may still be of experimental interest.

III. TWO-PHOTON EXCITATION OF ELECTRONS

We shall evaluate the two-photon transition rate of electrons from band 1 to band 3 in the vicinity of the threshold for cascade transitions. The calculations are made with the following assumptions: The beam with frequency Ω may be arbitrarily intense whereas the intensity of the beam with frequency ω is weak so that the transition rate is proportional to its intensity. At steady-state conditions, the transition rate at a given point in $\vec{K}$ space is given

by the probability of an electron to be at this particular point in band 3, $\rho_{33}(\vec{K})$ divided by the lifetime τ of the electron in this state. $\rho_{33}(\vec{K})$ is evaluated by solving the equations of motion of the density matrix.

Since the conditions postulated here are the same as those used by Yacoby,[3] we shall use the notation and part of the results obtained there. Using the same approximations we obtain

$$\rho_{33}(\vec{K})\tau^{-1} = \frac{\xi_{12}\xi_{23}\tau^{-1}}{1+S_{23}^2+4\xi_{23}}\left(\frac{2(1-iS_{13})+(1+iS_{23})}{(1-iS_{13})(1-iS_{12})+\xi_{23}}+\text{c.c.}\right), \tag{3}$$

where

$$\xi_{12} = (e/2m)^2 |\langle\Phi_1|(\vec{P}\cdot\vec{A})|\Phi_2\rangle|^2 (T^2/\hbar^2), \tag{4}$$

$$\xi_{23} = (e/2m)^2 |\langle\Phi_2|(\vec{P}\cdot\vec{B})|\Phi_3\rangle|^2 (T^2/\hbar^2). \tag{5}$$

$\vec{A}$ and $\vec{B}$ are the vector potentials of the beams with frequency equal to ω and Ω, respectively. Φ_i is the Bloch function of the ith band, and T is the off-diagonal relaxation time. S_{12}, S_{13}, and S_{23} are given by

$$S_{12} = (\hbar\omega - \epsilon_{12})T/\hbar, \tag{6}$$

$$S_{13} = (\hbar\omega + \hbar\Omega - \epsilon_{13})T/\hbar, \tag{7}$$

$$S_{23} = (\hbar\Omega - \epsilon_{23})T/\hbar. \tag{8}$$

The total transition rate R of electrons to band 3 is given by the integral over all possible $\vec{K}$ values.

Let us first evaluate the transition rate per unit volume for the case that the surfaces F_{12} and F_{23} are spheres. In this case the energy differences which appear in the integral depend only on $|\vec{K}|$. On the other hand, the matrix elements of $(\vec{P}\cdot\vec{A})$ and $(\vec{P}\cdot\vec{B})$ do not depend on $|\vec{K}|$ but do depend on the direction of $\vec{K}$. In this case it is convenient to express the integral in spherical coordinates:

$$R = (1/4\pi^3)\int d\varphi \int d(\cos\theta)\int |\vec{K}|^2 d|\vec{K}|\,\rho_{33}(\vec{K})\tau^{-1}. \tag{9}$$

Since the integral is proportional to ξ_{12} and ξ_{12} is independent of $|\vec{K}|$, it can be taken out of the integral with respect to $|\vec{K}|$. In this case the integral with respect to $|\vec{K}|$ denoted by R' depends on φ and θ only through the dependences of ξ_{23} on φ and θ. We can therefore express the transition rate in the following way:

$$R = (1/4\pi^3)\int d\xi_{23}\, g(\xi_{23})\int |\vec{K}|^2 d|\vec{K}|\,[\rho_{23}(\vec{K})\tau^{-1}/\xi_{12}], \tag{10}$$

where $g(\xi_{23})$ is a weighting function independent of $\hbar\omega$. The function $g(\xi_{23})$ is complicated and depends on the specific band structure of the material, therefore it will not be evaluated here. However, a qualitative understanding of the dependence of R on $\hbar\omega$ may be obtained from the dependence of R' on $\hbar\omega$ and on ξ_{23}. R' has been numerically evaluated as a function of $\hbar\omega$ with two varying parameters. The results varying ξ_{23} as a parameter are shown in Fig. 1. The effective masses in this case have been chosen so that $\vec{\nabla}_{\vec{K}}\epsilon_{12}(\vec{K})$ and $\vec{\nabla}_{\vec{K}}\epsilon_{13}(\vec{K})$ have opposite directions. One observes that for values of $\xi_{23} \ll 1$ the results are proportional to ξ_{23} and therefore to the intensity of the beam with frequency equal to Ω. However, if ξ_{23} approaches unity or becomes larger than unity, the transition rate saturates and for values of ξ_{23} large enough the peak even splits. The dependence of R on $\hbar\omega$ is a weighted integral of R' with respect to ξ_{23}. One, therefore, expects that R will also saturate and split if the intensity of the Ω beam is large enough. The ratio between the peak value of R the transition rate to band 3 and the transition rate to band 2 for $\xi_{23} = 1$ is of the order of 1 : 250. The results varying m_3^* as a parameter are shown in Fig. 2. In calcu-

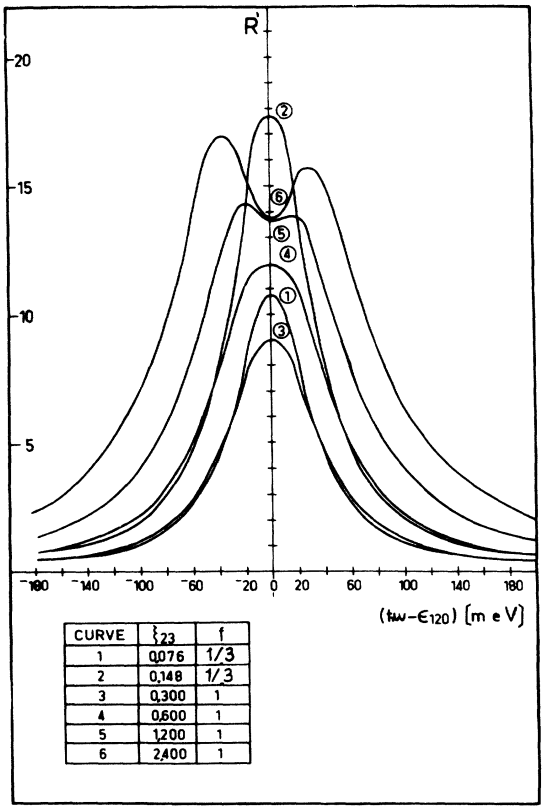
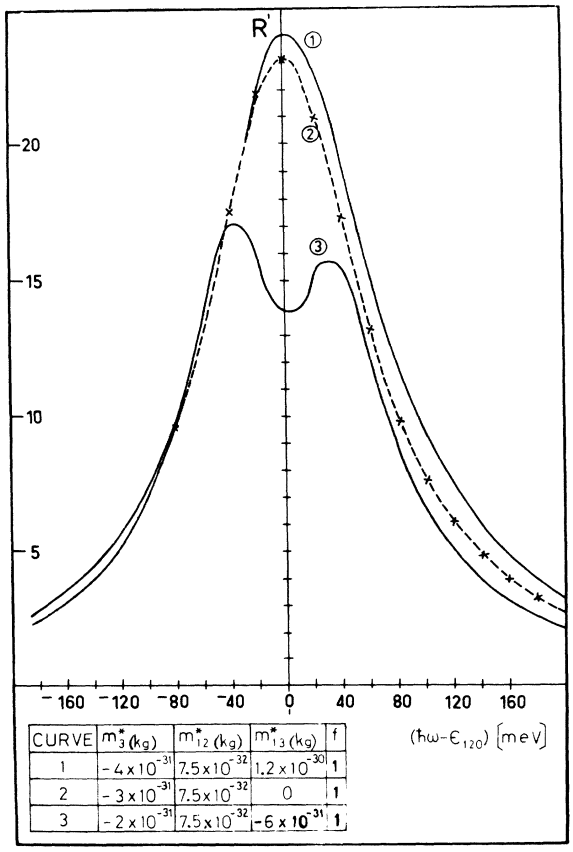


FIG. 1. Two-photon transition rate R' to band 3 as a function of $\hbar\omega - \epsilon_{120}$ and ξ_{23} as a parameter. The following conditions were assumed: Surfaces F_{12} and F_{23} are spheres; $\hbar\Omega = 1.8$ eV; $T = \tau = 2\times10^{-14}$ sec; $m_1^* = -3\times10^{-31}$ kg; $m_2^* = 10^{-31}$ kg; $m_3^* = -2\times10^{-31}$ kg. Consequently, $m_{12}^* = 7.5\times10^{-32}$ kg and $m_{13}^* = -6\times10^{-31}$ kg. The gap between bands 1 and 2 and the gap between bands 2 and 3 are $\epsilon_{g12} = 1.25$ eV and $\epsilon_{g23} = 2.42$ eV. The vertical coordinate is in arbitrary units. For the relative comparison of the curves, one should multiply the vertical coordinate of each curve by the appropriate f factor.



CURVE	m_3^* (kg)	m_{12}^* (kg)	m_{13}^* (kg)	f
1	-4×10^{-31}	7.5×10^{-32}	1.2×10^{-30}	1
2	-3×10^{-31}	7.5×10^{-32}	0	1
3	-2×10^{-31}	7.5×10^{-32}	-6×10^{-31}	1

FIG. 2. Two-photon transition rate R' as a function of $\hbar\omega - \epsilon_{120}$ and m_3^* as a parameter. The following conditions were assumed: Surfaces F_{12} and F_{23} are spheres, $\xi_{23}=2.4$, all other conditions are the same as in Fig. 1. The vertical coordinate is in arbitrary units. For relative comparison of the curves one should multiply the vertical coordinate of each curve by the appropriate numerical factor f.

lating curve 1 of this figure we took m_3^* to be equal to that used in Fig. 1. Then we decreased its absolute value so that the gradients of $\epsilon_{12}(\vec{K})$ and $\epsilon_{13}(\vec{K})$ reach the same direction. In so doing the combined effective mass of bands 1 and 2 remains constant and positive whereas the combined effective mass of bands 1 and 3 changes signs from a negative to a positive value. In this case one observes that the splitting of the peak disappears. The splitting of the peak and its dependence on the effective masses is explained in a way similar to the one used by Yacoby.[3] Schematic band diagrams are shown in Fig. 3. The energy of combined states of one electron and N or $N-1$ photons with energy $\hbar\Omega$ are illustrated as a function of $\vec{K}$. One observes that for certain values of $\vec{K}$ (in fact on surface F_{23}) the states $\langle(2, \vec{K}), N|$ and $\langle(3, \vec{K}), N-1|$ are degenerate. As a result of this, the energy bands split. Two cases are considered. (a) $m_{12}^*>0$ and $m_{13}^*>0$; in this case the gradients of $\epsilon_{12}(\vec{K})$ and $\epsilon_{13}(\vec{K})$ are in the same direction. (b) $m_{12}^*>0$ and $m_{13}^*<0$; in this case the gradients of $\epsilon_{12}(\vec{K})$ and $\epsilon_{13}(\vec{K})$ are in opposite directions. One observes that the transition from band 1 to the combined bands 2 and 3 absorbing a photon $\hbar\omega$ is allowed continuously if $\hbar\omega$ is larger than the minimum gap. On the other hand, such transitions are not allowed for photon energies near $\hbar\omega_0$. This gap in photon energy for which the transition is not allowed is reflected in the calculated transition-rate spectrum as a splitting of the peak. The fact that the transition rate between the peaks does not go to zero is due to relaxation.

Let us now consider the case that the surfaces F_{12} and F_{23} touch along a line. It is convenient in this case to perform the integral in $\vec{K}$ space in cylindrical coordinates,

$$R=(1/4\pi^3)\int d\varphi \int dK_s \int K_\perp\, dK_\perp\, \rho_{33}(\vec{K})\tau^{-1} \ . \quad (11)$$

Here K_s is the coordinate parallel to the radial axis whereas $K_\perp$ is perpendicular to it. If the bands involved in this case are not degenerate at $\vec{K}=0$, both S_{12} and S_{13} and the matrix elements will be independent of φ. In addition, in the vicinity of the line of contact where the main contribution to the integral is obtained, the matrix elements do not change as a function of K_s and $K_\perp$. The integrals with respect to K_s and $K_\perp$ have been performed numerically as a function of $\hbar\omega$ varying the same parameters which were varied in the previous case. The results with ξ_{23} as a parameter are shown in Fig. 4. Here again, the effective masses have been chosen so that the gradient with respect to $\vec{K}$ of $\epsilon_{12}(\vec{K})$ and $\epsilon_{13}(\vec{K})$ have opposite signs. One observes that the transition rate first rises to a peak at a photon energy slightly larger than the threshold photon energy and then it decreases and saturates. For values of ξ_{23} close to or larger than unity, the transition rate

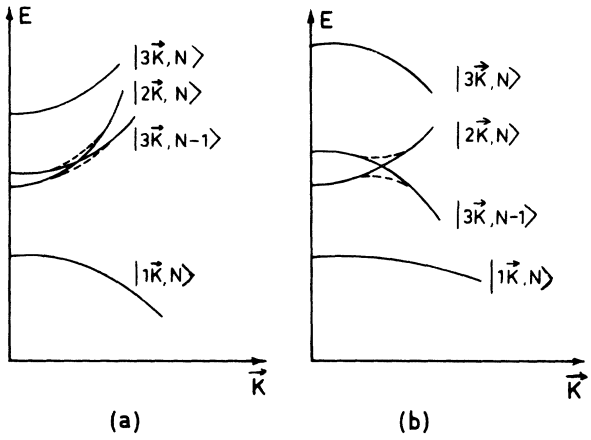


FIG. 3. Energy of combined electron-photon states as a function of K.

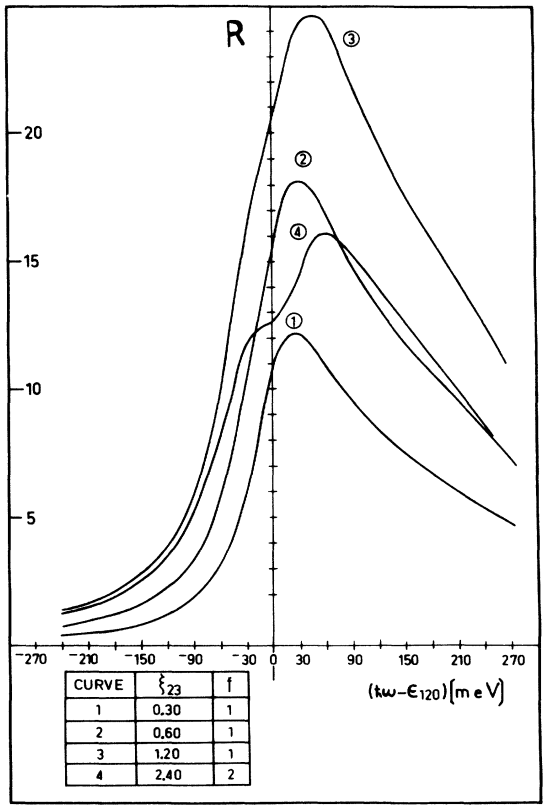


FIG. 4. Two-photon transition rate R as a function of $\hbar\omega - \epsilon_{120}$ and ξ_{23} as a parameter. The following conditions were assumed: Surfaces F_{12} and F_{23} are ellipsoids of revolution; $m^*_{12l} = 5 \times 10^{-31}$ kg; $m^*_{12t} = 10^{-30}$ kg; $m^*_{13l} = -10^{-30}$ kg; $m^*_{13t} = -2 \times 10^{-31}$ kg. The vertical coordinate is in arbitrary units. For the relative comparison of the curves one should multiply the vertical coordinate of each curve by the appropriate f factor.

at the peak saturates and the slope has again the form of a split peak. The ratio between the transition rate to band 3 and the transition rate to band 2 for $\xi_{23} = 1$ is of the order of 1 : 1000. The results with m_3^* as a variable parameter are shown in Fig. 5. Here again one observes that the splitting disappears when the effective masses are such that the gradients have the same direction. In general, surfaces F_{12} and F_{23} will at threshold touch in points. The contribution to the transition rate in the vicinity of threshold will come from points in $\vec{K}$ space close to the points of contact. Therefore the transition rate may be expressed in the following way:

$$R = \sum_m (1/4\pi^3) \int \rho_{33}^{(m)}(\vec{K}) \tau^{-1} \, d^3\vec{K} \, . \qquad (12)$$

The matrix elements will be different around different points of contact but will not change considerably in the vicinity of each point. We denote the contribution to the transition rate from points around m by $R^{(m)}$. Choosing the origin of a coordinate system to coincide with the point of contact, we obtain

$$R^{(m)} = (1/4\pi^3) \int d^2K_s \int dK_\perp \rho_{33}^{(m)}(\vec{K}) \tau^{-1} \, , \qquad (13)$$

where $K_\perp$ is the coordinate perpendicular to the surfaces at the point of contact and K_s are coordinates on the plane tangent to the two surfaces. This integral has been evaluated numerically and the results are shown in Fig. 6. We have performed this calculation for both beams being weak because saturation effects in this case are quite small. One observes that at threshold there is a sharp rise in the transition rate which then saturates towards a constant value. In fact, if one neglects relaxation and considers only weak intensities the transition rate has the form of a step function.

IV. TWO-PHOTON PHONON-ASSISTED TRANSITIONS

The expressions one obtains for evaluating TPPAT rates are very complex. For this reason we shall neglect the effect of relaxation on the functional dependence of the transition rate on $\hbar\omega$. We shall

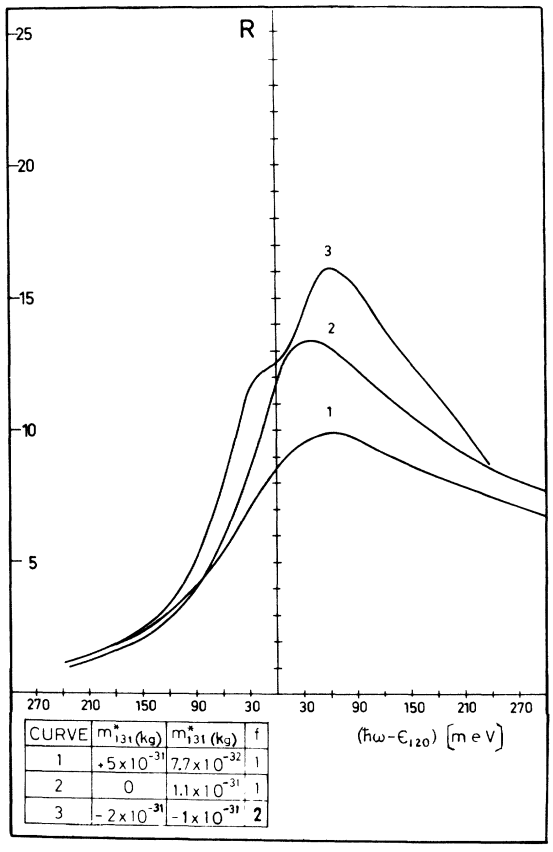


FIG. 5. Two-photon transition rate R as a function of $\hbar\omega - \epsilon_{120}$ and m^*_{13t} and m^*_{13l} as parameters. The condition assumed here is that the surfaces F_{12} and F_{23} are ellipsoids of revolution. $\xi_{23} = 2.4$ and all other conditions are the same as in Fig. 4.

further assume that both electromagnetic beams are weak. We shall focus our attention on the general case in which the surfaces F_{12}, F_2, and F_{23} touch in points. As discussed in Sec. II, there are two cases of interest: (a) Surfaces F_2, F_{12}, F_{23} have a common point of contact, and the dominant electron-phonon interaction is due to polar phonons. (b) Surface F_2 touches surfaces F_{12} and F_{23} in separate points while surfaces F_{12} and F_{23} have no points in common.

Case a

The transition rate of electrons from band 1 to band 3 is given by

$$R=(\tau^2/4\pi^3 8\pi^3)\int d^3K_1 \times\int d^3K_2\, P_{1\vec{K}_1\to 2\vec{K}_1} P_{2\vec{K}_1\to 2\vec{K}_2} P_{2\vec{K}_2\to 3\vec{K}_2}\,, \quad (14)$$

where τ is the lifetime of the electron, and $P_{n\vec{K}_i\to m\vec{K}_j}$ is the transition probability per unit time of an electron from a state in band n at the point $\vec{K}_i$ to a state in band m at the point $\vec{K}_j$. Making use of our assumptions, we obtain

$$P_{1\vec{K}_1\to 2\vec{K}_1}=(2\pi/\hbar)|d_{12}|^2\delta(\epsilon_{12}(\vec{K}_1)-\hbar\omega)\,, \quad (15)$$

$$P_{2\vec{K}_2\to 3\vec{K}_2}=(2\pi/\hbar)|d_{23}|^2\delta(\epsilon_{23}(\vec{K}_2)-\hbar\Omega)\,, \quad (16)$$

$$d_{12}=(e/2m)\langle\Phi_1|\vec{P}\cdot\vec{A}|\Phi_2\rangle\,,\qquad d_{23}=(e/2m)\langle\Phi_2|\vec{P}\cdot\vec{B}|\Phi_3\rangle\,, \quad (17)$$

$$P_{2\vec{K}_1\to 2\vec{K}_2}=(2\pi/\hbar)|\langle 1_{\vec{q}},\,2\vec{K}_2|\,H'_{ep}|0_{\vec{q}},\,2\vec{K}_1\rangle|^2 \times\delta(\epsilon_2(\vec{K}_1)-\epsilon_2(\vec{K}_2)-\epsilon_{\vec{q}})\,. \quad (18)$$

Here $\langle 1_{\vec{q}},\,2\vec{K}_2|$ is a product state of an electron in band 2 and at the point $\vec{K}_2$ and the first excited state of the optical vibrational mode with wave vector $\vec{q}$.

The electron-phonon perturbation is given by[4]

$$H'_{ep}=-4\pi ie\left[\frac{\epsilon_{\vec{q}}}{8\pi V}\frac{1}{4\pi\epsilon_0}\left(\frac{1}{\epsilon^{(\infty)}}-\frac{1}{\epsilon^{(0)}}\right)\right]^{1/2} \times\sum_{\vec{q}}\frac{1}{|\vec{q}|}(b_{\vec{q}}e^{i\vec{q}\cdot\vec{r}}+b^{+}_{\vec{q}}e^{-i\vec{q}\cdot\vec{r}})\,, \quad (19)$$

where $\epsilon^{(\infty)}$ and $\epsilon^{(0)}$ are the dielectric constants of the crystal for high and low frequencies, respectively, and $b^{+}_{\vec{q}}$ is the phonon-creation operator. Thus, the matrix element in Eq. (18) for given values of $\vec{K}_1$ and $\vec{K}_2$ can be expressed in the form

$$V_{\vec{K}_2,\vec{K}_1}=g/|\vec{K}_1-\vec{K}_2|\,. \quad (20)$$

Notice that g does depend on $\vec{K}_1$ and $\vec{K}_2$. However, the contribution to the integral in Eq. (14), for values of $\hbar\omega$ close to the threshold value, comes only from points $\vec{K}_1$ and $\vec{K}_2$ which are close to the point of contact of the three surfaces. Thus g may be considered approximately constant.

In order to evaluate the integrals we shall use the same coordinate system used in order to evaluate the two-photon transition rate in the general case. Let us expand the energy differences $\epsilon_{12}(\vec{K})$ and $\epsilon_{23}(\vec{K})$ and the energy $\epsilon_2(\vec{K})$ in terms of these coordinates:

$$\epsilon_{12}(\vec{K})=\epsilon_{120}+aK_s^2+uK_\perp\,, \quad (21)$$

$$\epsilon_{23}(\vec{K})=\hbar\Omega-cK_s^2-vK_\perp\,, \quad (22)$$

$$\epsilon_2(\vec{K})=\epsilon_{20}+dK_s^2+bK_\perp\,. \quad (23)$$

The requirement that there be a threshold for TPPAT imposes certain restrictions on the coefficients. At threshold the surfaces F_{12} and F_{23} are expressed close to the point of contact by the equations

$$aK_s^2+uK_\perp=\epsilon_{\vec{q}}u/b \quad\text{and}\quad cK_s^2+vK_\perp=0\,,$$

respectively. The energy ϵ_2 at a point $\vec{K}_1$ on surface F_{12} is given by

$$\epsilon_2(\vec{K}_1)=\epsilon_{20}+dK_{s1}^2-K_{s1}^2\,ba/u+\epsilon_{\vec{q}}\,. \quad (24)$$

Similarly the energy ϵ_2 at a point $\vec{K}_2$ on surface F_{23} is given by

$$\epsilon_2(\vec{K}_2)=\epsilon_{20}+dK_{s2}^2-K_{s2}^2\,bc/v\,. \quad (25)$$

F_{12} and F_{23} are the surfaces corresponding to threshold if for any $\vec{K}_1$ and $\vec{K}_2$,

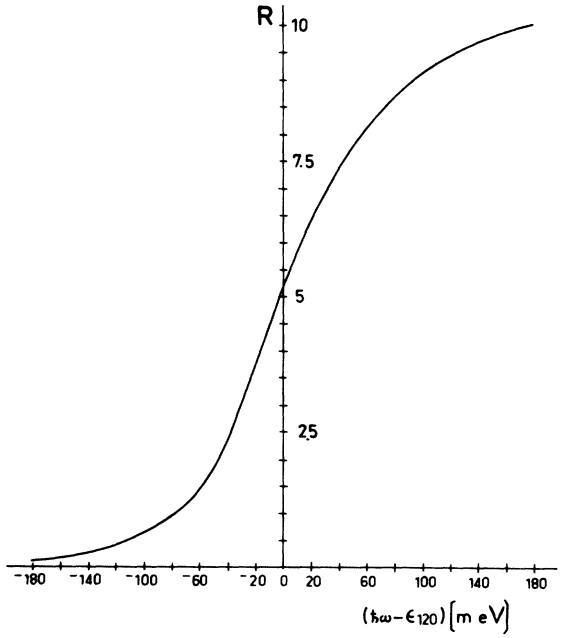


FIG. 6. Two-photon transition rate R as a function of $\hbar\omega-\epsilon_{120}$. The following conditions were assumed: Surfaces F_{12} and F_{23} touch in points.

$$\epsilon_2(\vec{K}_1) - \epsilon_2(\vec{K}_2) \leq \epsilon_{\vec{q}} .$$

The constraints imposed in this case on the coefficient are

$$d - ab/u < 0 , \tag{26}$$

$$d - bc/v > 0 . \tag{27}$$

The transition rate R is expressed in terms of the coordinates K_s and $K_\perp$ in the following form:

$$R = (\tau^2/4\pi^3 8\pi^3)(2\pi/\hbar)^3 |d_{12} g d_{23}|^2 I , \tag{28}$$

and

$$I = \int \tfrac{1}{2} dK_{s1}^2 \tfrac{1}{2} dK_{s2}^2 dK_{\perp 1} dK_{\perp 2} d\varphi_1 d\varphi_2 [K_{s1}^2 + K_{s2}^2 + (K_{\perp 1} - K_{\perp 2})^2 - 2K_{s1}K_{s2}\cos(\varphi_1 - \varphi_2)]^{-1}$$

$$\times \delta(\bar{\epsilon} - aK_{s1}^2 - uK_{\perp 1}) \delta(d(K_{s1}^2 - K_{s2}^2) + b(K_{\perp 1} - K_{\perp 2}) - \epsilon_{\vec{q}}) \delta(cK_{s2}^2 + vK_{\perp 2}) \tag{29}$$

and $\bar{\epsilon} = \hbar\omega - \epsilon_{120}$. The integrals with respect to φ_1 and φ_2 are immediate and lead to the result that

$$I = \tfrac{1}{2}\pi \int dK_{s1}^2 dK_{s2}^2 dK_{\perp 1} dK_{\perp 2} \{[K_{s1}^2 + K_{s2}^2 + (K_{\perp 1} - K_{\perp 2})^2]^2 - 4K_{s1}^2 K_{s2}^2\}^{-1/2} 2\pi$$

$$\times \delta(\bar{\epsilon} - aK_{s1}^2 - uK_{\perp 1}) \delta(d(K_{s1}^2 - K_{s2}^2) + b(K_{\perp 1} - K_{\perp 2}) - \epsilon_{\vec{q}}) \delta(cK_{s2}^2 + vK_{\perp 2}) . \tag{30}$$

Integrating over $K_{\perp 1}$ and $K_{\perp 2}$, we obtain

$$R = (\tau^2/2\pi u v C \hbar^3) |d_{12} g d_{23}|^2$$

$$\times \int_0^{K_{s0}} K_{s2} [F^2(K_{s2}) - G^2(K_{s2})]^{-1/2} dK_{s2} , \tag{31}$$

where

$$A = d - bc/v; \quad C = ba/u - d;$$

$$\epsilon = b(\hbar\omega - \epsilon_{120})/u - \epsilon_{\vec{q}} ;$$

$$F(K_s) = (\epsilon - Ak_s^2)/C + K_s^2$$

$$+ [\epsilon_{\vec{q}}/b + dK_s^2/b - d(\epsilon - AK_s^2)/bc]^2 ;$$

$$G(K_s) = 2K_s[(\epsilon - AK_s^2)/C]^2 ; \quad K_{s0} = (\epsilon/A)^{1/2} .$$

The last integral has been numerically evaluated and results for a specific case are given in Fig. 7. In order to present the results in a way that they can be compared to the two-photon transition rate, τ was estimated in the following way: According to our assumption the relaxation is mainly due to electron–polar-phonon interaction, thus

$$\tau^{-1} \cong (8\pi^3)^{-1} \int d^3K_2 P_{2\vec{K}_1 - 2\vec{K}_2} . \tag{32}$$

In carrying out this calculation g was assumed to be independent of $\vec{K}_1$ and $\vec{K}_2$. This assumption is, of course, not quite accurate. However, it helps us obtain an order of magnitude. From the upper limit of the integral in Eq. (31) one finds that the threshold energy for TPPAT is given by

$$\hbar\omega = \epsilon_{120} + u\epsilon_{\vec{q}}/b . \tag{33}$$

This threshold energy is larger than the threshold energy for two-photon transitions by $u\epsilon_{\vec{q}}/b$. For energies larger than this threshold, the transition rate rises sharply although not as a step and then saturates to a value which is of the same order of magnitude as the two-photon transition rate. When the surfaces F_{12} and F_{23} are approximately spheres and relaxation is neglected the two-photon transition rate has as a function of $\hbar\omega$ the form of a sharp peak. If one neglects the dependence of $\epsilon_{\vec{q}}$ on $\vec{q}$ the TPPAT rate has also the form of a sharp peak shifted in energy by

$$\epsilon_{\vec{q}} m_2^*/m_{12}^* .$$

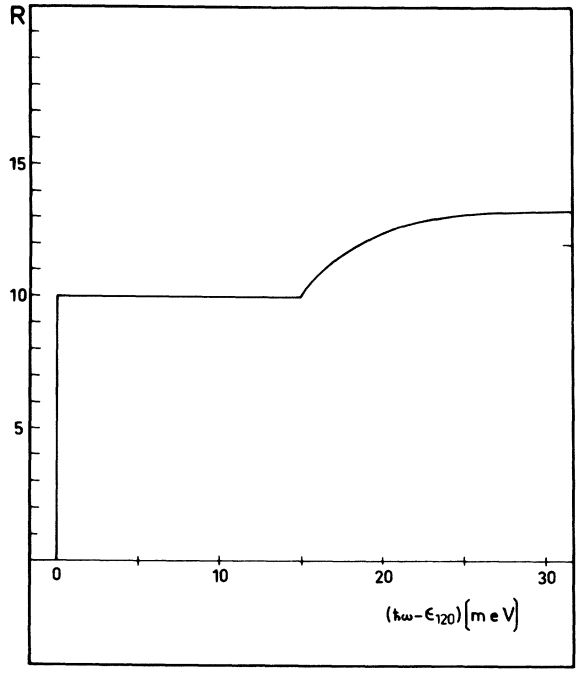


FIG. 7. Sum of the two-photon and TPPAT rate as a function of $\hbar\omega - \epsilon_{120}$, the phonon energy $\epsilon_{\vec{q}} = 30$ meV. The parameters of the expansion of $\epsilon_{12}(\vec{K})$ and $\epsilon_{23}(\vec{K})$ are $a = 10^{-37}$ J m^2; $b = 2\times10^{-28}$ J m; $c = 2\times10^{-38}$ J m^2; $d = 6\times10^{-38}$ J m^2; $u = 10^{-28}$ J m; $v = 2\times10^{-28}$ J m.

(In this case the approximation is a good one because F_{12} and F_{23} are approximately spheres in a region, in $\vec{K}$ space, very small compared to the Brillouin zone.) The effect of the relaxation on the functional dependence of the transition rate on $\hbar\omega$ will be to broaden the peaks to the order of $\Delta\omega \approx 2\tau^{-1}$.

Case b

The transition rate in this case is again given by Eq. (14). The main contribution to the integral is obtained in the vicinity of the two points of contact. We, therefore, expand the energies ϵ_{12} and ϵ_2 in the vicinity of their point of contact in terms of the coordinates K_{s1} and $K_{\perp 1}$ which are tangent and perpendicular, respectively, to the surfaces at the point of contact. Assuming for simplicity cylindrical symmetry, we obtain

$$\epsilon_{12}(\vec{K}) = \epsilon_{120} + aK_{s1}^2 + uK_{\perp 1} , \tag{34}$$

$$\epsilon_2(\vec{K}) = \epsilon_{20} + d_1 K_{s1}^2 + b_1 K_{\perp 1} . \tag{35}$$

Similarly, we expand ϵ_{23} and ϵ_2 around their points of contact:

$$\epsilon_{23}(\vec{K}) = \hbar\Omega - cK_{s2}^2 - vK_{\perp 2} , \tag{36}$$

$$\epsilon_2(\vec{K}) = \epsilon_{20} + d_2 K_{s2}^2 + b_2 K_{\perp 2} . \tag{37}$$

In order that there be a threshold the following inequalities should be satisfied

$$d_1 - ab_1/u < 0 , \tag{38}$$

$$d_2 - cb_2/v > 0 . \tag{39}$$

The transition rate can then be expressed in the form

$$R = \tau^2(2\pi/\hbar)^3 \left| d_{12} V_{\vec{K}_2,\vec{K}_1} d_{23} \right|^2 I/(4\pi^3 8\pi^3) , \tag{40}$$

where

$$I = \int \tfrac{1}{4} dK_{s1}^2 dK_{s2}^2 dK_{\perp 1} dK_{\perp 2} d\varphi_1 d\varphi_2 \delta(\bar{\epsilon} - ak_{s1}^2 - uK_{\perp 1}) \times \delta(d_1 K_{s1}^2 - d_2 K_{s2}^2 + b_1 K_{\perp 1} - b_2 K_{\perp 2} - \epsilon_{\vec{q}}) \delta(cK_{s2}^2 + vK_{\perp 2}) . \tag{41}$$

Integrating over φ_1, φ_2, $K_{\perp 1}$, and $K_{\perp 2}$, we find that

$$I = (\pi^2/uv) \int dK_{s1}^2 dK_{s2}^2 \delta(K_{s1}^2(d_1 - ab_1/u) - K_{s2}^2(d_2 - cb_2/v) - \epsilon_{\vec{q}} + \bar{\epsilon} b_1/u) . \tag{42}$$

This expression is then exactly integrated and found to be

$$I = \frac{\pi^2}{uv} \frac{b_1 \bar{\epsilon}/u - \epsilon_{\vec{q}}}{(ab_1/u - d_1)(d_2 - b_2 c/v)} . \tag{43}$$

One therefore observes that in this case the TPPAT rate is linear in $\bar{\epsilon} = \hbar\omega - \epsilon_{120}$.

V. SUMMARY AND CONCLUSIONS

The two-photon transition rate of electrons from valence to conduction band without and with phonon assistance has been evaluated as a function of the photon energy of one of the beams. It has been shown that the two-photon transition rate without phonon assistance undergoes strong changes in the vicinity of the energy corresponding to the threshold for two-photon cascade transitions. This threshold takes place when the surfaces F_{12} and F_{23}, corresponding to the photon energies $\hbar\omega_0$ and $\hbar\Omega$ of the two beams, touch each other. In the general case when the two surfaces touch at points, the transition rate has the form of a distorted step. When the two surfaces touch along a line, the transition rate has the form of a peak, one side of which decreases to a finite value, whereas in the case that the surfaces are spheres the transition rate has the form of a peak. For low-intensity beams the transition rate is, of course, proportional to the intensity of each of the beams. When the intensity of one of the beams is increased to values such that ξ_{23} becomes equal to or larger than unity the intensity of the transition rate saturates. Moreover, if the combined effective masses m_{12}^* and m_{13}^* have opposite signs, the transition rate in the case of spherical surfaces splits into two peaks. A less pronounced effect is found when the surfaces touch along a line.

The TPPAT rate has been shown to be of interest in two cases:

Case a. The surfaces F_{12}, F_{23} and F_2 have a common point of contact and the dominant interaction of electrons with phonons is with polar phonons. In this case the transitions rate rises sharply for photon energies close to the threshold photon energy and then saturates to a value smaller, but of the same order of magnitude, as the two-photon transition rate.

Case b. Surface F_2 touches surfaces F_{12} and F_{23} in different points. In this case the transition rate is proportional to the difference

$$\hbar\omega - \hbar\omega_0 - \epsilon_{\vec{q}} u/b_1 .$$

Measurement of the transition rate as a function of $\hbar\omega$ may yield some useful information about the band structure. At threshold the photon energies $\hbar\omega_0$ and $\hbar\Omega$ of the two beams are equal to the energy differences between bands 1 and 2 and between bands 2 and 3, respectively, at the same point in $\vec{K}$ space. This point is the point of contact between the two surfaces F_{12} and F_{23} and in most cases will be on a line of high symmetry. This information can, of course, be compared directly with theoretical band-structure calculations. The information obtained in this way is similar to that obtained from measuring the intensity of a parametric beam close to the threshold for double resonance. However, measurement of the transition rate is not limited to crystals with inversion symmetry nor to cases for which the gradients of $\epsilon_{12}(\vec{K})$ and $\epsilon_{13}(\vec{K})$ have oppo-

site directions at the point of contact.

As pointed out in Sec. IV, the energy difference between the threshold for two-photon transition and for TPPAT is equal to $u\epsilon_{\vec{q}}/b$. u and b are equal to the absolute values of the gradients of $\epsilon_{12}(\vec{K})$ and $\epsilon_2(\vec{K})$, respectively, near the point of contact of the surfaces F_{12}, F_{23}, and F_2. Since in this case $\vec{q}$ is very small, $\epsilon_{\vec{q}}$ is, in most cases, known either from ir or Raman measurements. Thus, measurement of the transition-rate spectrum may yield the ratio u/b which can be directly compared to theoretical band-structure calculations.

The actual determination of the transition rate of electrons to band 3 is, of course, a lot more difficult than the measurement of the parametric beam. However, in cases where band 3 does not have points in common with band 2, it can be carried out in the following way:

Electrons which have been excited to band 3 will cascade to a local minimum in this band. From here they will make transition to the almost empty conduction band—band 2. Provided that radiative transitions are allowed by symmetry at this point, the transition will be predominantly radiative. The photon energy of the fluorescent light is equal to the energy gap between bands 2 and 3 at the local minimum energy point in band 3. Thus, measurement of the intensity of the fluorescent light at the appropriate wavelength as a function of $\hbar\omega$, will yield the desired spectrum.

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Application of the Method of Lattice Statics to Carbon Interstitials in α-Iron†

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The method of lattice statics has been applied to determine the strain-field displacements about single octahedral and tetrahedral carbon interstitials in α-iron as well as the strain-field interaction energies between pairs of octahedral interstitials. A comparison of the exact lattice-statics displacements to the corresponding results of an asymptotic lattice-statics calculation indicates that elasticity theory is not valid closer than $25a$ from the octahedral interstitial in either the [100] or [011] direction in the lattice, where a is half of a cubic unit-cell side. The lattice-statics displacements have also been compared to analogous results obtained from a direct-space calculation, and some differences between the two sets of results are apparent. Relaxation energies have been calculated for the two types of carbon interstitial, and the octahedral configuration is found to be the more stable of the two. Assuming the tetrahedral configuration to be the saddle point for interstitial migration, the migration energy is found to be 0.27 eV.

I. INTRODUCTION

Since the advent of the high-speed digital computer, it has become possible to perform theoretical calculations to determine the properties of crystal lattices containing point defects. In particular, given a reasonably reliable expression for the interatomic potential between the atoms of the lattice, one can obtain numerical results for the energy change, volume change, and atomic displacements associated with the creation or migration of vacancies or host-atom–type interstitials within the lattice.

The most common approach to this type of problem is to treat the defect as though it were surrounded by a small crystallite of host atoms, each of which is permitted to move as a discrete particle and allowed to interact by means of pairwise interatomic potentials. The remainder of the crystal is treated as an elastic continuum. The displacements of the discrete atoms surrounding the defect are found by minimizing the energy in the crystallite