error with the calculated values z_{av} taking the quantization into account. This over-all agreement is not obtained with the calculations without quantization.

(ii) A lower dopant N_A in the bulk causes a less steep potential well at the surface and increases z_{av}, as is seen from comparison of curves 2 with 4, 3 with 5, and 6 with 7.

(iii) Applying a forward bulk bias also decreases the steepness of the potential well and increases z_{av}; a negative bias does the reverse. Compare curve 1 with 2 and with 3, 4 with 5.

(iv) The difference between calculations of z_{av} with and without quantization being taken into account is less pronounced the less steep is the potential well and the higher the temperature. In the case of curve 4 the measurements do not enable us to distinguish between quantized or not quantized electrons. The energy separation of the quantized levels in this case is of the order of kT. If a negative bias is applied (curve 5) or the temperature lowered (curve 6), the distinction can clearly be made.

To sum up, the quantization of electrons in silicon inversion layers has been experimentally verified at 77 and 300 °K. All previous experimental work on this quantization has been done at temperatures of 4.2 °K and lower.

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Nonlinear Response of Bound Electrons to X Rays

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In the high-frequency limit, general expressions for second- and third-order induced electronic current densities in a medium are derived. These are valid for any medium with arbitrary spatial electronic-density variations. It is shown that the second-order current density at x-ray frequencies depends directly on the gradient of the unperturbed electronic density, so that it is sensitive to density variations both near the surface and near the ionic cores in a solid.

Recently, Eisenberger and McCall[1] have observed x-ray parametric conversion due to the lowest-order nonlinearity in a solid. This was proposed earlier by Freund and Levine.[2] They also considered theoretically the case of mixing of an intense optical wave with a wave at x-ray frequency.[3] Furthermore, an amplifier at such a high frequency leading to the availability of highly intense and monochromatic x-ray sources now seems to be a distinct possibility. It is, therefore, of some interest to examine critically the calculation of nonlinear susceptibilities of a solid at x-ray frequencies. Although, Eisenberger and McCall[1] and Freund and Levine[2] have tried to derive expressions for the second-order susceptibility in a solid at x-ray frequencies, we find that their results are not general enough to include the very significant effect due to the potential barrier at the surface of the solid.

Since x-ray photon energies are much higher than the surface barrier, we may argue that the effect of the surface should be negligible. However, in the high-frequency limit ($\hbar\omega \gg E_B$, where E_B is a typical electronic excitation energy for dominant transitions), we will show that the second-order current density is proportional to the gradient of the unperturbed electronic density. Thus it is a direct measure of its spatial variations. It is sensitive not only to the periodic density variations near the ionic cores in a solid, but also to the variation near the surface. In centrosymmetric solids, like metals, it has already been shown by Jha[4] that the surface plays an important role in determining the second-order nonlinearity even at optical frequencies. Experimentally this has been verified[5] beyond any doubt.

A self-consistent formulation for a nonrelativistic calculation of the induced linear and nonlinear current densities in a solid, which is valid for *arbitrary* spatial variations of the induced fields, has been given by Jha and Warke (to be referred to as I).[6] This can be used for all those frequencies for which $\hbar\omega \ll mc^2$. To be complete, if we also include the spin-orbit coupling of the electrons in the medium, which was ignored by Jha and Warke, the linear current density $\vec{J}_A$, the bilinear current density $\vec{J}_{AA}$, and the trilinear current density $\vec{J}_{AAA}$ may be directly obtained from Eqs. (3.26) to (3.31) of I with

$$\mathcal{H}_A(\omega) = \frac{e}{mc} \sum_{\vec{q}} e^{i\vec{q}\cdot\vec{r}}\, \vec{a}(\vec{q}, \omega) \cdot \vec{P}(\vec{q}), \tag{1}$$

$$\mathcal{H}_{AA}(\omega_1 + \omega_2) = \frac{e^2}{2mc^2}\, \vec{a}(\omega_1) \cdot \vec{a}(\omega_2), \tag{2}$$

$$\vec{J}_0^{\mathrm{op}}(\vec{Q}) = \frac{e^{-i\vec{Q}\cdot\vec{r}}}{L^3} \left(\frac{-e}{m}\right) \vec{P}(-\vec{Q}), \tag{3}$$

$$\vec{J}_A^{\mathrm{op}}(\vec{Q}, \omega) = \frac{e^{-i\vec{Q}\cdot\vec{r}}}{L^3} \left(\frac{-e^2}{mc}\right) \vec{a}(\omega), \tag{4}$$

$$\vec{P}(\vec{q}) = \vec{p} + \frac{\hbar\vec{q}}{2} + \hbar(\vec{s} \times \vec{q}) + \frac{\hbar}{2mc^2}(\vec{s} \times \vec{\nabla} V), \tag{5}$$

where $\vec{a}$ is the self-consistent vector potential, $\vec{s}$ is the electronic spin, $\vec{p}$ is the momentum operator, and V is a general single-particle potential in which the electron is supposed to be moving in the medium. The unperturbed states $|\,\alpha\rangle$ in I are now the eigenstates of the Hamiltonian

$$\mathcal{H}_0 = \frac{p^2}{2m} + V(\vec{r}) + \frac{\hbar}{2m^2c^2}(\vec{s} \times \vec{\nabla} V) \cdot \vec{p}, \tag{6}$$

with eigenvalues E_α.

From the expressions for the current densities in I we observe that incident and generated frequencies ω_i appear in the energy denominators in the form $1/(E_B - \hbar\omega_i - i\epsilon)$. In the high-frequency limit, when $\hbar\omega_i \gg E_B$, we keep terms only to the lowest-order in this parameter. However, we do not use this expansion when ω_i is of the order of an optical frequency or less, for example, when we consider the case of difference-frequency generation with $\hbar\omega_1 - \hbar\omega_2 \approx E_B$. The results for such a calculation for $\vec{J}_A$, $\vec{J}_{AA}$, and $\vec{J}_{AAA}$ are given below.

I. LINEAR CURRENT DENSITY $\vec{J}_A$

In the high-frequency limit we obtain the well-known result

$$\vec{J}_A(\vec{Q}, \omega_1) = \frac{-e^2}{mc} \sum_{\vec{Q}_1} \vec{a}(\vec{Q}_1, \omega_1)\, n(\vec{Q} - \vec{Q}_1), \tag{7}$$

where $n(\vec{Q} - \vec{Q}_1)$ is the Fourier transform of the unperturbed electronic density $n(\vec{r})$, with $n(\vec{q} = 0) = n$, the number of electrons per unit volume. For a periodic system $\vec{J}_A(\vec{Q}, \omega_1)$ is nonvanishing only if $\vec{Q} - \vec{Q}_1 = \vec{G}$, where $\vec{G}$ is a reciprocal-lattice vector. A field with wave vector $\vec{Q}_1$ thus gives rise to fields with wave vector $\vec{Q}_1 + \vec{G}$, which may be obtained by solving appropriate Maxwell's equations. In general, the self-consistent linear current density may be rewritten in the form

$$\vec{J}_A(\vec{r}, \omega_1) = (ie^2/m\omega_1)\, \vec{E}_1(\vec{r})\, n(\vec{r}), \tag{8}$$

where

$$\vec{E}_j(\vec{r}) = (i\omega_j/c)\, \vec{a}(\omega_j). \tag{9}$$

II. SECOND-ORDER CURRENT DENSITY $\vec{J}_{AA}$

For ω_1, ω_2, and $\omega_1 + \omega_2 \gg E_B/\hbar$, our consideration leads to

$$\vec{J}_{AA}(\vec{r}, \omega_1 + \omega_2) = \frac{-ie^3}{m^2\omega_1\omega_2} \left(\frac{n(\vec{r})\vec{\nabla}(\vec{E}_1(\vec{r}) \cdot \vec{E}_2(\vec{r}))}{2(\omega_1 + \omega_2)} + \frac{\vec{E}_2(\vec{r})\vec{\nabla} \cdot (\vec{E}_1(\vec{r})n(\vec{r}))}{\omega_1} + PDF \right), \tag{10}$$

where *PDF* implies terms obtained by permutations of distinct frequencies. Note that this differs from the corresponding expressions given in Refs. 1 and 2 for crystal, since they have not treated the surface correctly. Our expression is valid for an arbitrary variation of the unperturbed electronic density $n(\vec{r})$, whether in a crystal or in a liquid. In fact, by using Maxwell's equation,

$$\vec{\nabla} \times (\vec{\nabla} \times \vec{E}_1) - \frac{\omega^2}{c^2}\vec{E}_1 = \frac{4\pi i\omega_1}{c^2}\vec{J}_A(\vec{r}, \omega_1), \tag{11}$$

the bilinear induced polarization may be written in this case in the form

$$\vec{P}^{NL}(\vec{r}, \omega_1 + \omega_2) = \gamma_{12}\vec{\nabla}(\vec{E}_1 \cdot \vec{E}_2) + \beta_{12}(\vec{\nabla} \cdot \vec{E}_1)\vec{E}_2 + PDF, \tag{12}$$

where

$$\gamma_{12}(\vec{r}) = \frac{e^3 n(\vec{r})}{2m^2\omega_1\omega_2(\omega_1 + \omega_2)^2}, \tag{13}$$

$$\beta_{12} = \frac{e}{4\pi m\omega_2(\omega_1 + \omega_2)}\ . \tag{14}$$

This has exactly the same form as Jha's equation[4] for $\vec{P}^{NL}$ due to conduction electrons at optical frequencies. The second term in Eq. (12) is nonzero at the surface even for the primary field corresponding to $\vec{G}=0$.

In the case of difference-frequency mixing, when $\omega_{12}=\omega_1-\omega_2 \sim E_B/\hbar$, $\omega_1, \omega_2 \gg E_B/\hbar$, we find

$$\vec{J}_{AA}(\vec{Q}, \omega_{12}) = \frac{-e^3}{2m^2c^2}\Bigg(\sum_{\vec{Q}_1,\vec{Q}_2} \vec{a}_1(\vec{Q}_1)\cdot\vec{a}_2^*(\vec{Q}_2)\,\frac{1}{L^3} \times\sum_{\alpha\alpha'}\langle\alpha'|\,e^{i\vec{Q}_2\cdot\vec{r}}\,|\alpha\rangle\langle\alpha|\,e^{-i\vec{Q}\cdot\vec{r}}\vec{P}(-\vec{Q})|\alpha'\rangle \times\frac{f(E_{\alpha'})-f(E_\alpha)}{E_{\alpha'}-E_\alpha-\hbar\omega_{12}-i\epsilon}+PDF\Bigg), \quad (15)$$

where $f(E_\alpha)$ is the Fermi distribution function.

For the case when one of the incident frequencies, say, $\omega_1=\omega_0$, is an optical frequency with $\hbar\omega_0 \sim E_B$, $\hbar\omega_2 \gg E_B$, we obtain

$$\vec{J}_{AA}(\vec{r}, \omega_0+\omega_2) = \frac{-ie^2}{4\pi m\omega_2}\,\vec{E}_2(\vec{r})[\vec{\nabla}\cdot\vec{E}_0(\vec{r})], \quad (16)$$

which describes optical mixing,[1,2] and which will control parametric amplification of x-ray by an optical pump wave.

III. THIRD-ORDER CURRENT DENSITY $\vec{J}_{AAA}$

For all relevant frequencies large, Eq. (3.28) of I leads to

$$\vec{J}_{AAA}(r, \omega_1+\omega_2+\omega_3) = \frac{ie^4}{2m^3\omega_1\omega_2\omega_3}\Bigg(\frac{\vec{E}_3(\vec{r})\vec{\nabla}\cdot\{n(\vec{r})\vec{\nabla}[\vec{E}_1(\vec{r})\cdot\vec{E}_2(\vec{r})]\}}{(\omega_1+\omega_2)^2}+\frac{n(\vec{r})\vec{\nabla}[\vec{E}_3\cdot\vec{\nabla}(\vec{E}_1\cdot\vec{E}_2)]}{(\omega_1+\omega_2)(\omega_1+\omega_2+\omega_3)} +\frac{\vec{\nabla}(\vec{E}_1\cdot\vec{E}_2)\vec{\nabla}\cdot[n(\vec{r})\vec{E}_3]}{(\omega_1+\omega_2)\,\omega_3}+\frac{\vec{E}_3(\vec{r})\vec{\nabla}\cdot\{\vec{E}_2\vec{\nabla}\cdot[\vec{E}_1 n(\vec{r})]\}}{(\omega_1+\omega_2)\,\omega_1}+PDF\Bigg). \quad (17)$$

Similarly, the intensity-dependent part of the dielectric function may also be calculated. One finds

$$\vec{J}_{AAA}(\vec{q}_1-\vec{q}_1+\vec{q}_1, \omega_1-\omega_1+\omega_1) = \frac{ie^4n}{2m^3\omega^5}\,\vec{E}_1(\vec{q}_1)\cdot\vec{E}_1(\vec{q}_1)\,\vec{E}_1^*(\vec{q}_1)\,q_1^2, \quad (18)$$

so that for a plane-polarized wave

$$\frac{\Delta\epsilon(\vec{q}, \omega)}{\epsilon^L(\vec{q}, \omega)} = -\frac{4\pi n e^4}{2m^3\omega_1^4c^2}\,|E(\vec{q}, \omega)|^2. \quad (19)$$

Since this is negative, there is no self-focusing effect for x-rays.

From the preceding results it becomes clear that in the x-ray region one may obtain simple expressions for the linear as well as nonlinear current densities, which are valid for arbitrary variations of the electronic density in a medium. In particular, the lowest-order nonlinearity is a direct measure of its spatial variations in the medium. The electromagnetic interaction terms involving the spin-moment and spin-orbit coupling do not play any important role unless one is considering the difference-frequency mixing experiment in which $\hbar\omega_1-\hbar\omega_2$ is comparable to the typical excitation energy E_B. A more detailed account of this work will appear elsewhere.

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