here have implications for the interpretation of the near infrared spectrum of oxygen in silicon and these implications will be discussed elsewhere.[6]

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PARAMETRIC CONVERSION OF X RAYS

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We consider frequency conversion of x rays via the nonlinear interaction of short-wavelength radiation with crystalline solids. Phase-matched parametric down-conversion of Mo $K\alpha$ in diamond is computed to be observable with presently accessible sources.

The incoherent process of double Compton scattering, first discussed by Heitler and Nordheim,[1] in which a proton when interacting with a relativistic (and hence nonlinear) electron decays into two photons of lesser energy, is well known. We discuss here an analogous coherent phenomenon, the spontaneous parametric decay of x rays. This process is related to double Compton scattering in the same way that ordinary Bragg diffraction relates to ordinary Compton scattering, and is just one of a wide range of coherent nonlinear phenomena which, extensively studied in the optical region,[2] must exist also in the x-ray region of the spectrum. We emphasize here the parametric conversion of x rays because we find this new effect to be observable with available x-ray sources.

Many of the properties of spontaneous parametric conversion may be understood on the basis that this process arises as a result of the beating of the quantum fluctuations of the vacuum field with the input field. We accordingly begin our discussion by considering in the short-wavelength limit the parametric mixing of two waves in a nonlinear crystal. A semiclassical, nonrelativistic formalism is employed and we present here a discussion of only the situation in which all frequencies lie well above the K absorption edge of the medium; resonance effects and their associated phase shifts are not included.

Consider summation of two waves at frequencies ω_1 and ω_2 in a nonlinear crystal to produce a third wave at ω_3. In each atom of the crystal there is induced a small nonlinear polarization, $\mathcal{P}(\omega_3)$, which we write as

$$\mathcal{P}(\omega_3)=\beta(\omega_3=\omega_1+\omega_2)E(\omega_1)E(\omega_2) \tag{1}$$

with $E(\omega_i)$ the field amplitude at ω_i. The amplitude of the radiated field at ω_3 at some remote distance R is

$$E(\omega_3)=\frac{\omega_3^2}{Rc^2}E(\omega_1)E(\omega_2)\textstyle\sum_a\beta(\vec{r}_a)e^{-i\vec{K}\cdot\vec{r}_a}, \tag{2}$$

where

$$\vec{K}\equiv\vec{k}_3-(\vec{k}_1+\vec{k}_2). \tag{3}$$

$\vec{r}_a$ is the position vector of atom a, $\vec{k}_i$ is the wave vector of the field at ω_i, and the sum is over all atoms in the illuminated region of the crystal. Expanding β as a Fourier series in terms of the set of reciprocal lattice vectors of the crystal $\vec{Q}(hkl)$, we have

$$\sum_a\beta(\vec{r}_a)e^{-i\vec{K}\cdot\vec{r}_a}=\sum_{hkl}\sum_{\text{cells}}G(hkl)e^{i[\vec{Q}(hkl)-\vec{K}]\cdot\vec{r}_{\text{cell}}}, \tag{4}$$

where the nonlinear structure factor $G(hkl)$ is

$$G(hkl)=\sum_n g_n(hkl)e^{-2\pi i(hu_n+kv_n+lw_n)} \quad (5)$$

with u_n, v_n, w_n, the fractional coordinates of atom n in the cell, and the sum is over all atoms in the cell. The nonlinear atomic scattering factors $g(hkl)$ are the amplitudes of the Fourier components of β. The sum in Eq. (4) attains its maximum value when all unit cells radiate in phase; this occurs when for some reciprocal lattice vector

$$\vec{\kappa}_3=\vec{\kappa}_1+\vec{\kappa}_2+\vec{Q}(hkl) \quad (6)$$

which is the law of nonlinear diffraction.[3]

We proceed now to an expression for the nonlinear atomic scattering factor. To calculate this we employ the results from second-order time-dependent perturbation theory given by Armstrong et al.[4] for the coherent, nonlinear response of an atom to applied electromagnetic fields. The induced nonlinear polarization at the sum frequency may be written

$${}_\perp\vec{\mathcal{P}}(\omega_3)=\mathrm{Re}\left[\frac{e^3E(\omega_1)E(\omega_2)}{2m^2c\omega_1\omega_2\omega_3}e^{-i\omega_3 t}({}_\perp\vec{U}+{}_\perp\vec{B})\right]. \quad (7)$$

The left subscript $\perp$ implies the projection of $\vec{\mathcal{P}}$ (and other vectors) perpendicular to $\vec{\kappa}_3$; only this part radiates into the far field and is of interest to us here. Defining unit vectors $\hat{u}_i$ along the field directions $E(\omega_i)$, and components of the gradient operator $\nabla_i=\hat{u}_i\cdot\nabla$, and writing Schrödinger's equation as $\hbar\omega_{jg}|j\rangle=\mathcal{H}|j\rangle$, where $\mathcal{H}$ is the unperturbed Hamiltonian, we have

$${}_\perp\vec{U}=c\left\{{}_\perp\hat{u}_2\left\langle 0\left|e^{i(\vec{\kappa}_2-\vec{\kappa}_3)\cdot\vec{r}}\left(\frac{2\hbar^2\omega_1}{\mathcal{H}^2-\hbar^2\omega_1^2}\right)e^{i\vec{\kappa}_1\cdot\vec{r}}\nabla_1\right|0\right\rangle+\text{similar terms in }(1,2,3)\right\},$$

and

$${}_\perp\vec{B}=-\frac{\hbar c}{m}\left\{\left\langle 0\left|e^{-i\vec{\kappa}_3\cdot\vec{r}}\,{}_\perp\nabla\left(\frac{\hbar^2}{\mathcal{H}^2-\hbar^2\omega_3^2}\right)e^{i\vec{\kappa}_1\cdot\vec{r}}\nabla_1\left(\frac{2\hbar\omega_3\mathcal{H}}{\mathcal{H}^2-\hbar^2\omega_2^2}\right)e^{i\vec{\kappa}_2\cdot\vec{r}}\nabla_2\right|0\right\rangle+\text{similar terms in }(1,2,3)\right\}, \quad (8)$$

where

$$\frac{1}{1-(\mathcal{H}/\hbar\omega)^2}\equiv 1+\sum_{n=1}^{N-1}(-1)^{n+1}\left(\frac{\mathcal{H}}{\hbar\omega}\right)^{2n}+(-1)^{N+1}\frac{(\mathcal{H}/\hbar\omega)^{2N}}{1-(\mathcal{H}/\hbar\omega)^2}, \quad (9)$$

and the wave functions are assumed real. The dominant contribution arises from ${}_\perp\vec{U}$ and the first term on the right-hand side of Eq. (9), and is simply

$${}_\perp\vec{\mathcal{P}}(\omega_3)=g(hkl)\vec{\theta}_{312}(hkl)E(\omega_1)E(\omega_2), \quad (10)$$

where the nonlinear atomic scattering factor is

$$g(hkl)=\tau f(hkl),$$

with

$$\tau=e^3/2m^2c\omega_1\omega_2\omega_3,$$

the lowest order nonlinear correction to the Thomson scattering coefficient for electrons,[5] and $f(hkl)$ the linear atomic scattering factor. The vector $\vec{\theta}$ determines the polarization of the radiated field and is, in turn, determined by the geometry of the experiment:

$$\vec{\theta}_{312}(hkl)=\hat{v}_3\times\left[\hat{v}_3\times\left\{\frac{c}{\omega_3}(\hat{u}_1\cdot\hat{u}_2)\vec{Q}(hkl)-\frac{c}{\omega_1}[\hat{u}_1\cdot\vec{Q}(hkl)]\hat{u}_2-\frac{c}{\omega_2}[\hat{u}_2\cdot\vec{Q}(hkl)]\hat{u}_1\right\}\right]. \quad (11)$$

Here $\hat{v}_3$ is a unit vector along $\vec{\kappa}_3$, and Eq. (6) is assumed to be satisfied.

The derivation[4] of Eq. (7) is for a one-electron atom. We go over to a many-electron atom by taking $f(hkl)$ to be the well-known tabulated functions for such atoms.[6] It is now readily apparent that a large part of the theory of the linear diffraction of x rays,[7] including thermal factors, selection rules for (hkl), etc., may be directly incorporated into the corresponding theory of nonlinear phenomena.

We consider now in more detail spontaneous parametric decay, continuing the terminology employed in the microwave and optical region by calling the input beam the pump (p) and the two

output beams the signal (s) and idler (i). The equations of conservation of energy and momentum are

$$\omega_p = \omega_s + \omega_i,$$
$$\vec{k}_p + \vec{Q}(hkl) = \vec{k}_s + \vec{k}_i. \quad (12)$$

The theory of this process has been discussed by a number of authors[8]; of use here is the work of Kleinman[9] who does not tie his treatment to the optics of birefringent crystals, but shows generally that this phenomenon is completely described by the geometry of a "matching surface"—the locus of all points in $\vec{k}$ space for which Eqs. (12) are satisfied. Because the refractive index for x rays is so close to unity, the matching surface is very nearly an ellipsoid of revolution, a principal section of which is shown in Fig. 1. This surface has a finite "thickness," since even for a plane-wave, monochromatic pump the spread in the length of the $\vec{k}$ vector of the signal, $\delta\kappa_s$, for a fixed direction is $\delta\kappa_s \propto [\mathcal{L}K(\beta)]^{-1}$. Here $\mathcal{L}$ is the effective crystal length and $K(\beta) = 1-(\vec{\kappa}_s \cdot \vec{\kappa}_i/\kappa_s\kappa_i)$. The total signal power radiated into some solid angle $\Delta\Omega_s$ around $\vec{k}_s$ is proportional to $P_p\mathcal{L}^2\delta\kappa_s\Delta\Omega_s$, where P_p is the pump power, so that an enhancement in signal power is obtained when $\vec{k}_s$ and $\vec{k}_i$ are nearly parallel. This was called the "edge" enhancement by Kleinman, and for x rays corresponds to a choice of reciprocal lattice vector and crystal orientation such that one is near Bragg's angle for diffraction of the pump. We shall make use of this enhancement.

With this preliminary, we may, following Kleinman, write for the number of signal photons counted each second, $\dot{N}_s$,

$$\dot{N}_s = \frac{8\pi\omega_s{}^3\omega_i P_p \Delta\Omega_s}{c^4 K(\beta)}\mathcal{L}\left|\frac{G(hkl)}{v}\right|^2 \vec{\theta}_{spi}{}^2(hkl), \quad (13)$$

where v is the volume of a unit cell, and the last two factors form the square of the macroscopic nonlinear susceptibility.

We chose for numerical evaluation of Eq. (13) a geometry in which $\vec{k}_s$ and the $\vec{k}_i$ are approximately equal, separated, arbitrarily, by 20°, and arrayed more or less symmetrically about Bragg's angle for diffraction of the pump. Neglecting the small deviation from Bragg's angle θ_B, we have for an unpolarized pump

$$\theta_{spi}{}^2(hkl) = \vec{\theta}_{spi} \cdot \vec{\theta}_{spi}{}^* \cong (5/4)\sin^2(\theta_B). \quad (14)$$

In computing the effective crystal thickness $\mathcal{L}$, we assume the not necessarily optimum but simple geometry of a plane parallel slab oriented with

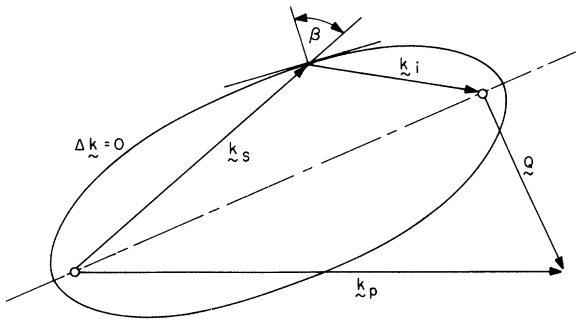

FIG. 1. Matching surface for parametric decay.

its external surfaces normal to the pump, whose aperture has a diameter much larger than the effective crystal thickness. The pump is attenuated upon passage into the crystal, and the signal is attenuated during passage out. This leads to an optimum crystal thickness t_{opt}, if the signal is emitted in the forward direction,

$$t_{opt} \cong \frac{\ln[\alpha_s/(\alpha_p\cos\varphi)]}{(\alpha_s/\cos\varphi)-\alpha_p},$$

and

$$\mathcal{L} \cong \alpha_p{}^{-1} z^{z/(1-z)}, \quad z = \alpha_s/\alpha_p\cos\varphi, \quad (15)$$

where the α's are the linear extinction coefficients, and φ is the angle the signal direction makes with respect to the forward normal to the slab. If the signal is emitted in the backward direction,

$$\mathcal{L} \cong [\alpha_p + \alpha_s/\cos\varphi]^{-1}, \quad (16)$$

where now φ is the angle the signal direction makes with the back-normal to the slab and where the slab thickness has been assumed much greater than $\mathcal{L}$. Assuming further a pump power[10] of 10 mW and $\Delta\Omega_s = 10^{-3}$ sr, we plot in Fig. 2 Eq. (13) as a function of the wavelength of the pump for the (004) reflection of diamond. This substance is chosen because of its high density, low loss, and availability in the form of nearly ideally perfect crystals.[11] Observe that with commonly available sources counting rates approaching one per second are anticipated. This is an easily detected signal provided only that background "noise" can be sufficiently reduced. We consider this problem next.

Most sources of noise, such as fluorescence, Compton scattering of the pump, etc., can be reduced by frequency discrimination techniques and, in fact, eliminated by simultaneously detecting, in fast time coincidence, both the signal and idler outputs; such a scheme is common in

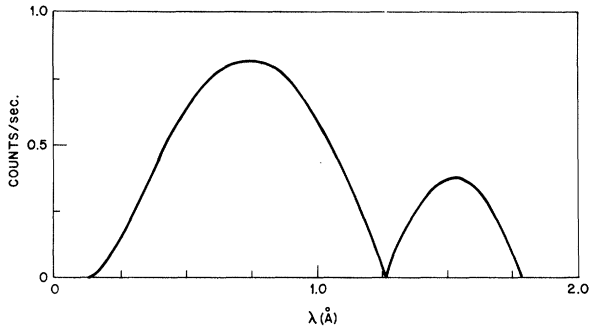

FIG. 2. Predicted counting rate for parametric decay as a function of the wavelength of the pump. The dip at ~1.25 Å is due to the signal being emitted parallel to the plate surfaces and being attenuated before it can exit. For wavelengths shorter than ~1.25 Å the signal is emitted in the forward direction, while for longer wavelengths emission is in the backward direction. Beyond ~1.79 Å the law of nonlinear diffraction can no longer be satisfied by the (004) reflection of diamond.

measurements of double Compton scattering but will not, in fact, eliminate double Compton scattering itself as a source of noise. The reason for this is that in the x-ray region only a small fraction of the pump energy, of order $\hbar\omega/mc^2$, is transferred to the electron. For free electrons the conservation equations and hence matching surface are practically the same as for parametric decay (the electron momentum replaces the reciprocal lattice vector $\vec{Q}$ in Fig. 1) and the two processes are difficult to separate. The expected number of double Compton photons emitted per second, $\dot{n}_s$, around the signal direction into a solid angle $\Delta\Omega_s$ and spectral bandwidth $\Delta\omega_s$, for which an idler photon is simultaneously emitted into a solid angle $\Delta\Omega_i$ around the idler direction is approximately[12]

$$\dot{n}_s \sim \frac{1}{\pi\hbar\omega_s}\left(\frac{e^2}{\hbar c}\right)\left(\frac{e^2}{mc^2}\right)^2\left(\frac{\hbar\omega}{mc^2}\right)^2 \times NP_p \frac{\Delta\Omega_s}{4\pi}\frac{\Delta\Omega_i}{4\pi}\frac{\Delta\omega_s}{\omega_s}, \qquad (17)$$

where N is the number of electrons. Evaluating Eq. (17) for 1-Å x rays, a pump power of 10 mW, $\Delta\Omega_s = \Delta\Omega_i = 10^{-3}$ sr, and $\Delta\omega_s \sim \omega_s(\Delta\Omega_s)^{1/2}\tan\beta$, and assuming all electrons to be free, we find $\dot{n}_s \sim 3\times10^{-3}$ count/sec, which is two to three orders of magnitude smaller than the expected counting rate for parametric decay.

We conclude by noting that there are many experiments capable of observing the parametric decay of x rays. The particular one we have described employs a relatively broad signal spectrum, convenient for a scintillation detector for example, in a comparatively narrow solid angle. By choosing $\vec{Q}$ equal to $-\vec{k}_p$ the same counting rate in a larger solid angle but very narrow spectral range is available, much reduced counting rates are, of course, easily measured, allowing the use of weaker x-ray sources, smaller or more highly absorbing crystals, and so forth. Observation of this effect appears well within the range of current technology and should permit the first measurements of coherent x-ray nonlinearities.

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