Parametric Down Conversion of X Rays into the Extreme Ultraviolet

Haim Danino and Isaac Freund
Department of Physics, Bar-Ilan University, Ramat-Gan, Israel
(Received 15 December 1980)

Using the 002 reflection of a LiF single crystal, we have observed phase-matched parametric down conversion of 8-keV (Cu-*Kα*) x rays into single photons at 7.7 keV; the corresponding idler photons are in the extreme vacuum ultraviolet at 335 eV. Agreement well within the estimated experimental uncertainty is found with theory, which predicts that this process can provide a means for the direct determination of valence-electron charge distributions.

PACS numbers: 42.65.Cq, 61.10.Fr

We report first observations of the parametric down conversion of x rays into the extreme ultraviolet (XUV). This phenomenon is one of three related nonlinear x-ray processes which, although described theoretically about a decade ago,[1-5] have proven remarkably difficult to realize experimentally. These three processes involve down conversion of x rays into (i) a lower-energy portion of the x-ray spectrum,[1,2] (ii) the XUV region,[3] and (iii) the optical region.[4,5] Each such process is characterized by dependence upon a different material parameter, offers special possibilities for probing the structure of matter, and presents its own unique set of experimental problems.

X-ray → x-ray parametric down conversion was first discussed theoretically by Freund and Levine,[1] and subsequently was observed experimentally by Eisenberger and McCall.[2] Within the large experimental uncertainty, agreement was found with theory,[1] which predicts that in this process the relevant material parameter is the structure factor of the total electronic charge density.

In our present x-ray → XUV experiment we detect the 7.70-keV signal photons produced during the nonlinear interaction of 8.04-keV (Cu-*Kα*) pump photons with a single crystal of LiF. The 335-eV idler photon is not detectable because of intense sample absorption. The theory of this process[3] reveals that the relevant material parameter is the structure factor of the weakly bound valence electrons, so that the methods described here offer the possibility of a direct determination of this important property. As becomes apparent, within the large experimental uncertainty, here again agreement is found between theory and experiment.

The down conversion of x rays into the optical region is also of special interest. As was shown theoretically,[4,5] a measurement of this process permits a direct determination of the microscopic charge redistribution produced by an applied optical field; all the linear optical properties of matter are determined by this quantity. This difficult experiment still remains to be accomplished.

In the process of phase-matched x-ray parametric down conversion an input pump photon at frequency ω_p upon interacting with a suitably oriented crystalline sample decays into a lower-energy photon pair, the signal at ω_s and the idler at ω_i, such that both energy and momentum are conserved:

$$\omega_p = \omega_s + \omega_i, \tag{1a}$$

and

$$\vec{k}_p + \vec{Q}(hkl) = \vec{k}_s + \vec{k}_i. \tag{1b}$$

Here the $\vec{k}$'s are the wave vectors of the photon fields, and phase matching is obtained with the aid of one of the reciprocal-lattice vectors, $\vec{Q}(hkl)$, of the crystal.[6] The locus of all possible solutions of Eqs. (1) defines a surface in k space, the matching surface,[7] which in the absence of dispersion is an ellipsoid of revolution whose eccentricity is controllable by a simple rotation of the crystal.[1] In Fig. 1 we sketch the apparatus used, show a principal section of this ellipsoid, and define the geometry of our experiment. This particular geometry was chosen since it yields a narrow signal spectrum into a comparatively large solid angle,[3,4] thereby reducing the severity of a number of experimental problems and permitting a simple, straightforward analysis of the data.

The fundamental kinematical prediction of Eqs. (1), and hence the unique signature of the effect sought, is that for a given deviation $\Delta\theta_B$ of the crystal setting from the Bragg angle θ_B, a signal of predetermined energy $\hbar\omega_s$ is emitted at a particular angle φ_s. In our present experiment,

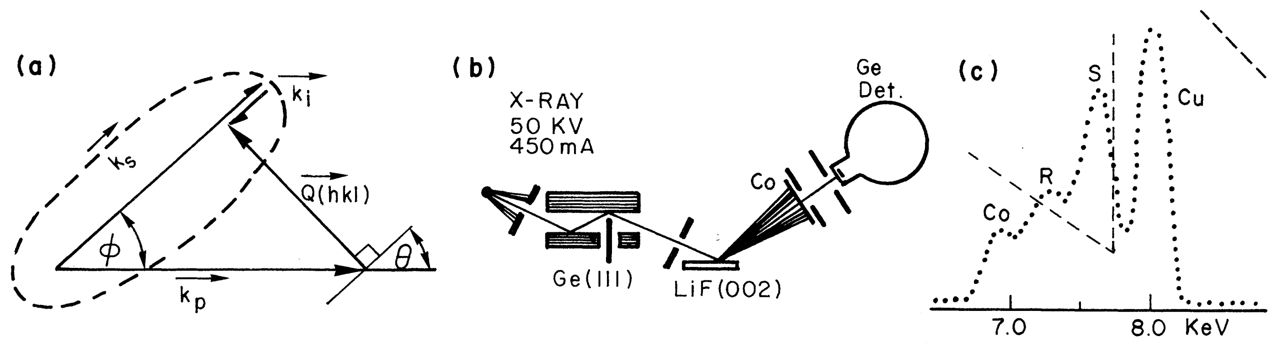

FIG. 1. (a) Wave-vector conservation diagram, Eq. (1), and elliptical matching surface (dashed line). (b) Experimental apparatus. The x-ray source is a commercial rotating anode device. (c) Spectrum measured during typical two-day counting period. The various spectral features are identified in the text. The dashed line shows the absorption of the Co filter in (b).

using the 002 reflection of LiF and $\hbar\omega_s = 7.70$ keV, $\Delta\theta_B = 6.7°$ and $\varphi_s = 46.8°$. Accordingly, three basic experimental measurements are performed. In each of these, two of the three parameters $\Delta\theta_B$, φ_s, and $\hbar\omega_s$ are fixed in turn, and the third is varied with a peak being sought at the correct value. A successful outcome to all three experiments, with the measured intensity being approximately the anticipated one, permits the claim made here that the phenomenon sought has indeed been observed.

The major experimental problem is the very small efficiency of the parametric down conversion, in the present experiment about 10^{-10}. Since the strongest x-ray process known is direct Bragg diffraction, which for our high-quality LiF crystal was measured to have an efficiency of $\sim 3 \times 10^{-2}$, a reasonable requirement is that the incident Cu-$K\alpha$ beam be free of parasitic radiation in the region of the signal at the 10^{-9}–10^{-10} level.[8] This was ultimately achieved by using a long channeled Ge monochromator with intermediate slit, as shown in Fig. 1. Verification of this degree of spectral purity is, of course, a nontrivial task.

Because of the weakness of the effect sought, a highly efficient intrinsic Ge energy-dispersive detector was used instead of a crystal spectrometer. Although the 150-eV resolution of this detector is adequate to separate the signal from Compton and thermally scattered pump, the intensity of these latter two processes is so great that they swamp the detector response. Accordingly, a Co filter was used to reduce the Compton and thermal scattering, which principally lie above the Co K absorption edge at 7.71 keV, while the signal falls directly below.

The spectrum of the radiation reaching the detector contains a number of features, as is indicated in Fig. 1. Visible there are attenuated peaks for the Compton and thermal scattering which blend into an unresolved feature labeled Cu, a peak containing the signal labeled S, the 690-eV fluorine Raman line labeled R, and $K\alpha$ fluorescence from the Co filter labeled Co. The signal peak is underlain by both the Co-$K\beta$ line with an intensity $\sim \frac{1}{3}$ that of the Co-$K\alpha$, and the tail of the Compton scattering. This tail extends, in fact, throughout the whole low-energy portion of the spectrum, at first falling off rapidly in intensity but ultimately diverging at zero energy.[9, 10] As becomes apparent, the effect of these two components, Co-$K\beta$ and the Compton tail, is to produce a smooth background to our measurements. We emphasize that the absolute intensities of all features appearing in this spectrum are quantitatively accounted for by a first-principles calculation, so that the instrumental response is well understood.

In Fig. 2 we plot for $\varphi_s = 46.8°$ and $\hbar\omega_s = 7.70$ keV the intensity of the signal peak as $\Delta\theta_B$ is varied. The dashed line is the calculated variation of the background. In performing this calculation the absolute intensity of the Compton tail at 7.70 keV is needed to an accuracy of better than 1%, but is available experimentally[11] only to an estimated uncertainty of 20%. Since Eqs. (1) predict no signal generation if $\Delta\theta_B$ is less than 6°, the data in this region are used to fix the amplitude of the Compton tail (the one adjustable parameter) to the required degree of accuracy. The presence of a peak with a maximum at ~7°, as

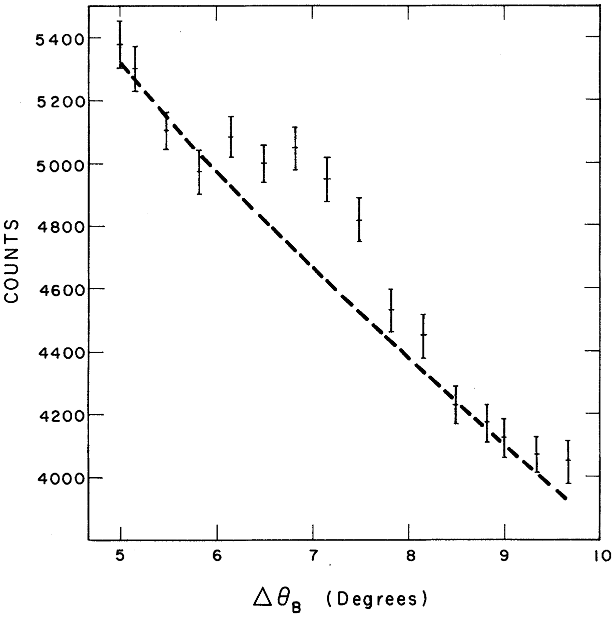

FIG. 2. Intensity of the signal peak (labeled S in Fig. 1.) vs $\Delta\theta_B$ for $\varphi_s = 46.8°$ and $\hbar\omega_i = 335$ eV. The dashed line is the calculated background whose variation is due principally to changing self-absorption in the rotating LiF crystal. Both the location and intensity of the peak at ~7° are in accord with the prediction of Ref. 3.

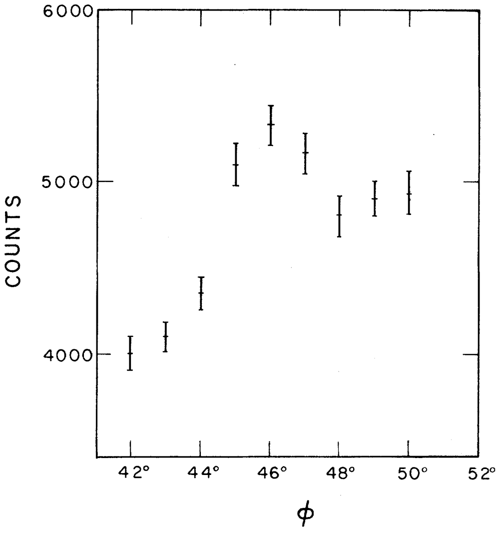

FIG. 3. Signal peak intensity vs φ (in degrees) for $\Delta\theta_B = 7.0°$ and $\hbar\omega_i = 335$ eV. The rising background, although in general accord with expectation, is not amenable to precise calculation which needs to include the variation with scattering angle of the Compton tail. This variation is not known to the required accuracy. The theory of Ref. 3 predicts that these data peak at $\varphi = 46.1°$ with an intensity ~20% greater than in Fig. 2. Both these expectations appear to be met.

anticipated, is quite evident.

In Fig. 3 we plot the signal intensity for $\Delta\theta_B = 7.0°$ as φ is varied. Here, again, a peak at the correct value ($\varphi_s = 46.1°$) is found. We also find that when φ_s and $\Delta\theta_B$ are properly set and the spectral bandwidth is scanned, the signal peaks at the appropriate place. Finally, other angular scans for combinations of φ and $\Delta\theta_B$ which are symmetric with Fig. 2 regarding thermal scattering ($\varphi = 43.2°$, $-5° \geqslant \Delta\theta_B \geqslant -9°$), but for which no signal is predicted, give the expected null results.

In the present experiment we have chosen $\hbar\omega_i$ to be less than the binding energy, $\hbar\Omega_K$, of the fluorine K shell, but greater than that of its L shell; as indicated in Ref. 3, this enhances the L shell response over that of the K shell by a factor of order $(\Omega_K/\omega_i)^2$. This enhancement occurs because the K-shell oscillator, being driven well below resonance, has a response proportional to $1/\Omega_K^2$, while the response of the L-shell oscillator, which is driven well above resonance, is proportional to $-1/\omega_i^2$. The parametric down conversion, itself, may be described as a Doppler shift of the pump photon scattered by the idler-driven atomic oscillators, with the appropriate idler field being supplied by vacuum fluctuations.[7]

The theory of Ref. 3 makes a quantitative prediction for the signal intensity in terms of a suitable nonlinear atomic scattering factor, which we write here as $g(hkl, \omega_i)$.[12] In Fig. 4 we compare theory (dashed line) with experiment using $|g(002; 335\text{ eV})|$ as the single adjustable parameter. For this we obtain a value of 6.9 with an estimated uncertainty of about 50% due to appreciable statistical fluctuations in the data points, uncertainties in the background of Fig. 2, and the difficulties inherent in absolute intensity measurements. A suitable theoretical value for Li^+F^- may be written as[3,13] $g(002; 335\text{ eV}) = (4.50 + 0.39i) + (1.78 + 0.12i) - 0.20$, where the first and second terms are the usual x-ray scattering factors, including dispersion,[14] for the fluorine L- and lithium K-shells,[15] and the last term is the fluorine K-shell contribution. We thus obtain $|g(002; 335\text{ eV})| = 6.1$, which agrees with the measured value to well within the estimated uncertainty. Accordingly, we anticipate that with suitable advances in instrumentation and technique, valence-electron charge densities may be directly determined by the method described here, without the need for the many complex and uncertain corrections which plague current approaches.[16]

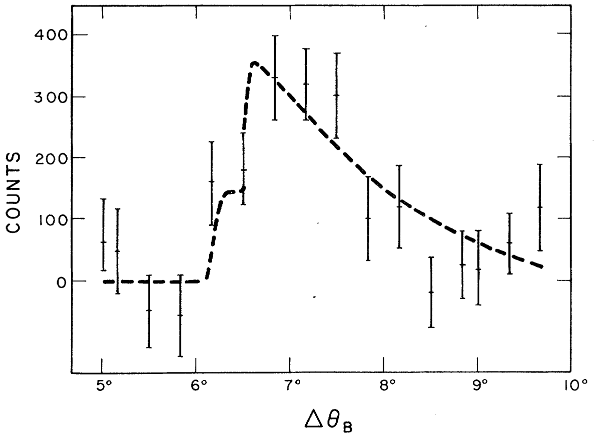

FIG. 4. Comparison of theory (dashed line) with experiment. The data are from Fig. 2 after subtraction of the calculated background. The step at 6.3° in the calculated curve arises from the presence of both α_1 and α_2 in the incident Cu-$K\alpha$ radiation, while the overall shape is determined by the $1/\omega_i{}^3$ dependence predicted by theory convolved with the instrumental transfer function. The nonlinear scattering factor of Ref. 3 is treated as a parameter (the only one), and is adjusted to yield the best fit. As indicated in Eqs. (2) and (5) of that text, the value so determined is within 15% of that obtained from a first-principles calculation.

We wish to thank Professor Joel Gertsten for the many conversations and calculations which played a vital role in the development of this work. We are also pleased to acknowledge stimulating discussions and supportive calculations by Professor N. Tzoar. This work was supported in part by the U. S.-Israel Binational Science Foundation, Jerusalem.

[1] I. Freund and B. F. Levine, Phys. Rev. Lett. 23, 854 (1969).

[2] P. Eisenberger and S. L. McCall, Phys. Rev. Lett. 26, 684 (1971).

[3] I. Freund, Chem. Phys. Lett. 12, 583 (1972).

[4] I. Freund and B. F. Levine, Phys. Rev. Lett. 25, 1241 (1970).

[5] P. Eisenberger and S. L. McCall, Phys. Rev. A 3, 1145 (1971). These authors consider the process of up conversion, rather than the down conversion discussed here.

[6] I. Freund, Phys. Rev. Lett. 21, 1404 (1968).

[7] D. A. Kleinman, Phys. Rev. 174, 1027 (1968).

[8] The effects of such parasitic radiation are further reduced by the fact that when the crystal is oriented so as to generate $\hbar\omega_s$ it does not satisfy the Bragg condition for this energy, nor is the detector at the proper location. Thermal scattering, however, is still a possibility.

[9] M. Gavrila, Phys. Rev. A 6, 1348 (1972), and 6, 1361 (1972).

[10] Y. B. Bannett, J. I. Gersten, N. Tzoar, and I. Freund, Phys. Rev. Lett. 36, 882 (1976).

[11] K.-F. Berggren, S. Manninen, T. Paakkari, O. Aikala, and K. Mansikka, in *Compton Scattering*, edited by B. Williams (McGraw-Hill, London, 1977), Table 6.6.

[12] We do not assume this to be simply the fluorine valence shell structure factor as was originally done in Eq. (11) of Ref. 3.

[13] I. Freund and B. F. Levine, Opt. Commun. 3, 101 (1971).

[14] R. W. James, *Optical Principles of the Diffraction of X-Rays* (Cornell Univ. Press, Ithaca, 1965), Chap. 4.

[15] *International Tables for X-Ray Crystallography*, edited by J. A. Ibers and W. C. Hamilton (Kynoch, Birmingham, 1974), Vol. IV, Sect. 2.2.

[16] Both the successes of, and problems with, current methods are reviewed by P. Coppens, in *Neutron Diffraction*, edited by H. Dachs (Springer-Verlag, Berlin, 1978), Chap. 3.