threshold of 6.0 eV and the excitation of acoustic modes of the lattice.

It may be significant that estimates indicate a pronounced band structure for motion parallel to the c axis with the first band edge occurring at a momentum corresponding to an energy of 5.9 eV for a free particle and a gap of 3.7 eV separating the first and second bands. A gap of this size would very effectively prevent an applied electric field from accelerating positrons in the first band back across the threshold for positronium formation.

Further experiments are planned which we hope will yield improved statistics.

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ELECTRODYNAMICAL BOND-CHARGE CALCULATION OF NONLINEAR OPTICAL SUSCEPTIBILITIES

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A simple model is proposed which relates the anharmonic motion of the bond charge to the higher order nonlinear susceptibilities. Excellent agreement with experiment is found for both the second- and third-harmonic coefficients.

For frequencies far above the lattice response, the dominant source of optical nonlinearities is the distortion of the electronic wave function. Previous calculations[1-3] of this electronic nonlinearity in semiconductors have been based on the static multipole moments of the ground-state charge distribution. They suffer from problems concerning the use of local-field corrections, and further, have only been done for a limited ionicity range, and only for the zinc-blende structure.

We propose a simple, electrodynamic model for the calculation of the second- and third-harmonic coefficients ($\chi_{2\omega}$ and $\chi_{3\omega}$), which automatically accounts correctly for most of the local-field effects, and which points out the crucial role played by the ionicity of the compound. Our model ascribes the nonlinear terms in the susceptibility to the anharmonic motion of bond charges q located approximately halfway between the two neighboring atoms. To show the generality of the theory both $\chi_{2\omega}$ and $\chi_{3\omega}$ are evaluated not only for the zinc-blende (z) semiconductors but also for the wurtzite (w), diamond (d), and rocksalt (r) structures covering the entire range of ionicity (i.e., Ge to LiF). Further, we calculate $\chi_{2\omega}$ for α quartz which has trigonal symmetry and two oxygen atoms per silicon atom. Excellent agreement with experiment is found.

The types of crystals we will now consider are d, z, w, and r. A good description[4-6] of these materials is given by a single average energy gap E_g, composed of a homopolar part E_h and a heteropolar part C, such that $E_g{}^2 = E_h{}^2 + C^2$. The values for E_h and C, given for a large number of crystals by Van Vechten,[6] are determined from the measured low-frequency linear susceptibility χ_ω, using $E_h = 40d^{-2.48}$ and the relation $\chi_\omega = (\hbar\Omega_p)^2/E_g{}^2$, where Ω_p is the plasma frequency which includes small corrections for d bands and other effects. The ionic energy gap is given by[5,6]

$$C = be^{-kR}\left(\frac{Z_\alpha}{r_\alpha} - \frac{Z_\beta}{r_\beta}\right)e^2, \tag{1}$$

where b is a constant close to 1.5 (for d, z, and w), e^{-kR} is the Thomas-Fermi screening constant, Z_α is the number of valence electrons on the α atom, r_α is the covalent radius of the α atom, and e is the electronic charge.

An applied electric field $\mathcal{E} = \mathcal{E}(t)$ will displace the bond charge q by a distance Δr and hence produce a polarization per unit volume of

$$P = \chi_\omega \mathcal{E} = \tfrac{3}{4}\sqrt{3}q\Delta r/d^3, \tag{2}$$

where $\tfrac{3}{4}\sqrt{3}d^{-3}$ arises from the number of bonds per cm^3 (in d, z, and w). From Eqs. (1) and (2) we see that this Δr will produce a change ΔC giv-

en to first order in Δr by

$$\Delta C = -\frac{16}{3\sqrt{3}}be^{-kR}\left(\frac{Z_\alpha + Z_\beta}{q}\right)e^2 d\chi_\omega \mathcal{E}$$

$$\equiv -\gamma e d\chi_\omega \mathcal{E}. \qquad (3)$$

In obtaining Eq. (3) we have used the fact that $\Delta r_\alpha = \Delta r_\beta$ and $r_\alpha \simeq r_\beta \simeq \frac{1}{2}d$. Setting $b = 1.5$, $e^{-kR} = 0.08$, $q = 0.50e$, and $Z_\alpha + Z_\beta = 8$, we find $\gamma = 6$.

Phillips' bond-charge theory[7] states that the magnitude of the bond charge q is $(2/\epsilon_h)e$ (ϵ_h is the homopolar part of the static dielectric constant ϵ). For an average zinc-blende crystal which is 50% covalent, $\epsilon_h = \frac{1}{2}\epsilon = 4$, giving $q_{av} = 0.50e$. For more ionic crystals, although $q > q_{av}$, it is less localized in the region between the two atoms. For more covalent crystals $q < q_{av}$, but $\mathcal{E}$ will displace somewhat more charge than simply q. Hence, we take $q = q_{av}$ as the appropriate value for the displaced bond charge.

The electric field $\mathcal{E}$ causes a shift ΔC which in turn changes the energy gap from E_g^2 to $[E_g(\mathcal{E})]^2 = E_h^2 + (C + \Delta C)^2$, and produces a variation from $\chi_\omega(0)$ to

$$\chi_\omega(\mathcal{E}) = \chi_\omega\left[1 - \frac{2C\Delta C}{E_g^2} - \frac{(\Delta C)^2}{E_g^2}\left(1 - \frac{4C^2}{E_g^2}\right)\right], \qquad (4)$$

where we have written $\chi_\omega \equiv \chi_\omega(0)$. The expansion of Eq. (3) to $O(\Delta r)^2$ also gives a term proportional to $\mathcal{E}^2$ and can be trivially included in the $(\Delta C)^2$ term in Eq. (4). However, except for extremely ionic materials, it is an order of magnitude smaller than the terms appearing in Eq. (4), and hence, to avoid unnecessary algebra, we neglect it.

Using Eq. (3) and picking out the coefficients of $\mathcal{E}$ and $\mathcal{E}^2$ in Eq. (4) [i.e., $P = \chi(\mathcal{E})\mathcal{E} = \chi_\omega\mathcal{E} + \chi_{2\omega}\mathcal{E}^2 + \chi_{3\omega}\mathcal{E}^3$], we can identify

$$\chi_{2\omega} = 2C\gamma e d\chi_\omega^2/E_g^2, \qquad (5a)$$

$$\chi_{3\omega} = \frac{\chi_{2\omega}^2}{\chi_\omega}\left(1 - \frac{E_g^2}{4C^2}\right). \qquad (5b)$$

Equation (5) gives the nonlinear susceptibilities of a single bond in terms of the linear susceptibility of that same bond. We can immediately interpret Eq. (5) in terms of macroscopic quantities if we now account for the geometry of the unit cell. Most of the necessary local-field corrections are automatically included when we interpret χ_ω as a macroscopic susceptibility since these corrections are absorbed into χ_ω. The ex-

pression we derive is valid for $2\omega < E_g$. For higher ω resonant enhancement of the susceptibilities must be taken into account. Rewriting Eq. (5) in terms of macroscopic susceptibilities, but using the same notation, yields

$$d_{ijk} = G_{ijk}(300)\gamma C d\chi_\omega^2/E_g^2, \qquad (6a)$$

where G_{ijk} is the geometrical factor.[8] For zinc-blende $G_{123} = 3^{-1/3}$, while for wurtzite $G_{333} = 2/9$, and $G_{113} = G_{311} = -\frac{1}{9}$. For z, w, d, and r structures

$$C_{1111} = \frac{(300)^2\gamma^2 d^2\chi_\omega^3}{E_g^2}\left(\frac{4C^2}{E_g^2} - 1\right) \text{ esu.} \qquad (6b)$$

The factors of 300 arise from the conversion of volts to electrostatic units. The units of C, E_h, and E_g are in electron volts, d is in centimeters. For the zinc-blende structure, Eq. (6a) gives the value d_{123} [i.e., using $\mathcal{E}(t) = \mathcal{E}\cos\omega t$ and $P_1(t) = 4d_{123}\mathcal{E}_2(t) + C_{1111}\mathcal{E}_1^3(t)$] and for wurtzite Eq. (6a) gives d_{333} [$P_3(t) = 2d_{333}\mathcal{E}_3^2(t)$].

Using the tabulated values for C and E_h,[8] $\gamma = 6$, and Eq. (6) we can easily determine d_{ijk} and C_{1111}. These values are given in Table I, where they are compared with experiment. We see that with no adjustable parameters we have achieved excellent agreement with experiment for d_{123}, d_{333}, d_{113}, and d_{311} over a wide range of ionicity. GaSb is 74% covalent while CdSe is 70% ionic.

It is interesting to determine Miller's delta[9] (defined below) since it normalizes out χ_ω and hence is more directly related to the intrinsic electronic distortion than is $\chi_{2\omega}$.[10-13] Defining $\Delta_{ijk} = d_{ijk}/\chi_\omega^3$ gives

$$\Delta_{ijk} = [G_{ijk}(300)\gamma d/(\hbar\Omega_p)^2]C \equiv C^*. \qquad (7)$$

To a good approximation both d and Ω_p are constant for these materials and hence Δ is closely proportional to C. In order to account for the small variation that does exist, and hence to show the true fit between theory and experiment, we have defined a new parameter C^*. For convenience we choose our units such that $C^* = C$ for GaSb and find that for these materials $C^* \simeq C$. Figure 1 is a plot of Eq. (7) and demonstrates the excellent agreement between theory and experiment.

Table I also shows that agreement for the third-harmonic coefficient C_{1111} is excellent in Ge, CdS, and LiF. The ionicity range varies from completely covalent in Ge to 99% ionic in LiF. There are no adjustable parameters (for LiF we

Table I. Comparison between theory and experiment. The letters in parentheses (d), (z), (w), and (r) refer to the diamond, zinc-blende, wurtzite, and rocksalt structures, respectively. Values listed are the average of all available data and the errors are standard deviations. For CdSe, the experimental d_{113} and d_{311} have been adjusted to be consistent with the average value of d_{333} given above. S. K. Kurtz has kindly made these references available prior to publication. See R. Beckman and S. K. Kurtz, "Second Harmonic Generation of Light in Crystalline Solids," in Landolt-Börnstein Numerical Data and Functional Relationships, edited by K.-H. Hellwege (Springer-Verlag, Berlin, Germany, to be published), New Series, Group I, Vol. 1.

Crystal (z)(43 m)	$d_{123}(10^{-7})$esu calculated	$d_{123}(10^{-7})$esu experimental
InSb	19	16.5 ± 3.5^{a}
GaSb	12	$14\pm2^{b,c}$
InAs	9.6	$11\pm1^{a,c,d}$
GaAs	5.7	$7.5\pm1.5^{a,c,d,e,f}$
GaP	3.4	$2.3\pm.5^{c,e,f,g}$
CdTe	3.5	4 ± 1.5^{d}
ZnTe	3.0	$3.1\pm.65^{a,d,f}$
ZnSe	1.4	$1.35\pm.35^{d,f}$
ZnS	0.85	$0.79\pm.2^{d,f}$
CuCl	0.32	$0.1\pm200\%^{i}$
BP	0.36	

Crystal (w)(6 mm)	d_{333} cal.	d_{333} exp.	$d_{113}=d_{311}$ cal.	d_{113} exp.	d_{311} exp.
(In Units of 10^{-7} esu)					
CdSe	2.6	$2.0\pm.7^{d,f}$	1.3	$1.15\pm.35^{f}$	$1.05\pm.35^{f}$
CdS	1.25	$1.0\pm.15^{d,h}$	0.60	$0.60\pm.09^{d,h}$	$0.55\pm.09^{d,h}$
ZnS	0.95	$.89\pm.3^{d,f}$	0.48	$0.50\pm.15^{d,f}$	$0.45\pm.15^{d,f}$
ZnO	0.25	$.22\pm.05^{e}$	0.12	$0.07\pm.025^{e}$	$0.07\pm.025^{e}$

Crystal (32)	d_{111} cal.	d_{111} exp.	d_{123} cal.	d_{123} exp.
(In Units of 10^{-9} esu)				
SiO$_2$	0.96	$1.15\pm.2^{j}$	0	$<.02^{k}$

Crystal	$C_{1111}(10^{-14})$esu calculated	$C_{1111}(10^{-14})$esu experimental
Ge(d)	16,000	$10,000\pm5,000^{l}$
Si(d)	5,300	600 ± 360^{l}
CdS(w)	250	160^{m}
LiF(r)	0.22	0.20^{m}

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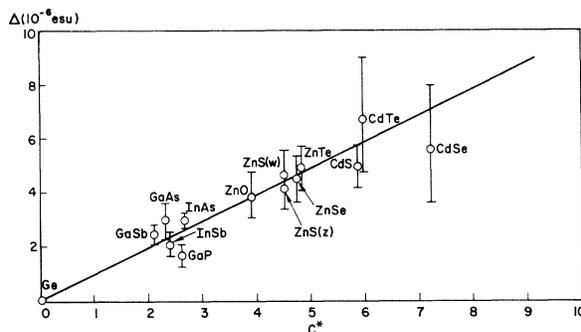[i]J. Jerphagnon, C. Schwab, and D. Chemia, Compt. Rend. B265, 1032 (1967).

FIG. 1. Plot of measured $\Delta_{123}=d_{123}/\chi_{\omega}{}^3$ for zinc blende or $\Delta_{333}=d_{333}/\chi_{\omega}{}^3$ for wurtzite, against the redefined C parameter $C*$. $C*$ is equal to the right-hand side of Eq. (7) (see text). The straight line is Eq. (7), i.e., $\Delta=C*$.

have also used $\gamma = 6$).

Equation (6) predicts that $C_{1111} = 0$ for $E_h/C = \sqrt{3}$. Of course, C_{1111} does not necessarily vanish since, as already mentioned, we have neglected the small contribution arising from the $(\Delta r)^2$ term. However, C_{1111} for GaSb ($E_h/C = 1.67$) should have an anomalously low value compared with InSb ($E_h/C = 1.48$) (the two compounds have otherwise similar properties).

As an example of the generality of this theory we can use Eq. (6a) to calculate the nonlinearity of α quartz. Quartz (SiO$_2$) has trigonal symmetry and two oxygen atoms per silicon atom. The geometrical factors of $G_{111} = 0.0814$ and $G_{123} = 0$ together with $\gamma = 6$ give the values for d_{111} and d_{123} shown in Table I. It is noteworthy that our theory, which neglects dispersion, gives $d_{123} = 0$ in agreement with Kleinman's[14] symmetry condition. The good agreement with experiment indicates that the bond-charge equilibrium position should be determined from the covalent radii r_α and r_β.

After completion of this manuscript, our attention was drawn to recent work by Flytzanis.[15] Without introducing the concept of the anharmonic bond-charge oscillator, Flytzanis[15] has derived similar results using the static multipole moments of the partially screened ions. In his model two disposable parameters are introduced

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to account for the coupling with the external field. Our model which has no adjustable parameters yields somewhat better agreement with experiment. Further, we calculate both $\chi_{2\omega}$ and $\chi_{3\omega}$ for the entire ionicity range (Ge to LiF) and for more general structures (i.e., SiO_2, wurtzite, and rocksalt).

Our calculation emphasizes the localized-bond[7] picture, whereas Phillips and Van Vechten[16] have done a related two-band random-phase–approximation description using bonding and antibonding states obtained from the dielectrically determined values of C and E_h.

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ISOMER SHIFT OF THE 123-keV GAMMA RAYS OF ^{154}Gd

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Isomer shifts of the $2^+ \to 0^+$ rotational transition in ^{154}Gd were determined in Mössbauer measurements. From comparison with isomer shifts in ^{156}Gd and ^{158}Gd, the ratios $\Delta \langle r^2 \rangle_{154}/\Delta \langle r^2 \rangle_{156} = +7.3 \pm 1.9$ and $\Delta \langle r^2 \rangle_{154}/\Delta \langle r^2 \rangle_{158} = +30 \pm 10$ are deduced. These ratios imply a considerable increase in rigidity for deformed nuclei above neutron number $N = 90$. The existing theoretical values are discussed.

The mean-square charge radii $\langle r^2 \rangle$ of rotating deformed nuclei are slightly affected by the Coriolis and centrifugal forces. These small changes $\Delta \langle r^2 \rangle$ between rotational states have recently become measurable by observing isomer shifts (I.S.) of recoilless γ rays[1-4] and energy shifts of γ rays from muonic atoms.[4,5] Isomer shifts of the 123-keV $2^+ \to 0^+$ rotational transition in ^{154}Gd were studied in order to investigate the change of deformation for a supposedly "soft" rotator in the transition region from weak to strong deformation. From the relative values of $\Delta \langle r^2 \rangle$ for $2^+ \to 0^+$ transitions in ^{154}Gd, ^{156}Gd,[4] and ^{158}Gd,[1] one finds convincing evidence of the transition from "soft" to "rigid" rotators between neutron number $N = 90$ and $N = 94$.

The transmission of recoilless γ rays through resonance absorbers was measured at 4.2°K as a function of the Doppler shift produced by moving the source sinusoidally with a feedback-regulated loudspeaker drive. Figure 1 shows transmission spectra of the 123-keV gamma rays from a ^{154}EuF$_3$ source through Gd$_2$O$_3$, GdAl$_3$, and GdFe$_2$ absorbers. Despite the extremely small resonance absorption in GdFe$_2$ (0.02%), a definite I.S. relative to Gd$_2$O$_3$ and GdAl$_3$ is observed. In order to exclude pseudoshifts simulated by line asymmetries, comparison I.S. measurements were performed with the 87-keV gamma rays of ^{155}Gd from Sm(^{155}Eu)Al$_3$ source. The I.S. for both transitions are compiled in Table I.

Figure 2 is a plot of the I.S. of the 123-keV line of ^{154}Gd vs the I.S. of the 87-keV line of ^{155}Gd for identical absorbers. In the absence of pseudoshifts, the points should be on a straight line, as is seen to be the case—well within experimental error. From the slope of the line, the ratio $\Delta \langle r^2(^{154}\text{Gd}) \rangle / \Delta \langle r^2(^{155}\text{Gd}) \rangle = -2.62 \pm 0.60$ is deduced. For the 87-keV gamma rays in ^{155}Gd, the I.S. between Gd metal and trivalent compounds was cali-