er resonances at intermediate frequencies between ω_L and ω_R. This seems to rule out the cascade process in Fig. 3(a).[8] The remaining processes, (b) and (c), will have resonance factors in perturbation theory of the form $(\omega_L - \omega_{\mathrm{ex}}{}^0)^{-1}(\omega_R - \omega_{\mathrm{ex}}{}^0)^{-1}$ that describe the propagation of the exciton just after creation and just before annihilation. Absorption and emission data indicate a strong broadening of the exciton line due to phonon interactions. Thus it is a much better approximation to replace the bare-exciton frequency $\omega_{\mathrm{ex}}{}^0$ in the propagators by the experimental exciton frequency ω_{ex} plus a large imaginary part $i\Gamma(\omega, T)$. This will give the type of broad resonance we need to explain our data, including temperature dependences of the type shown in Fig. 2.

It is necessary to assume no additional strong frequency dependences beyond those already accounted for. This might tend to favor the processes in Fig. 3(c) of Ref. 1 over those of Fig. 3(b), but this will require further study. Due to the exciton's kinetic energy, the integrals over the k vectors of the intermediate states of processes such as that of Fig. 3(b) of Ref. 1 should provide additional smoothing of the ω_L dependence beyond the substantial amount already provided by large exciton linewidths represented by $\mathrm{Im}\Sigma$.

In a more complete paper to be submitted shortly we shall discuss many more experimental details and hope to say more about the theory of this effect including how the above arguments relate to a more detailed treatment of the exciton-photon interaction.[9]

We are pleased to acknowledge several profitable discussions with R. W. Hellwarth, J. H. Marburger, and especially D. A. Kleinman.

---

*Work supported in part by the U. S. National Science Foundation.

†Permanent address: Department of Physics, University of Illinois, Urbana, Ill.

[1] R. C. C. Leite and S. P. S. Porto, Phys. Rev. Letters 17, 10 (1966).

[2] B. Tell, T. C. Damen, and S. P. S. Porto, Phys. Rev. 144, 771 (1966).

[3] See the contributions by E. Gutsche and J. Voigt, in *Proceedings of the International Conference on II-VI Semiconducting Compounds, Providence, R. I., 1967*, edited by D. G. Thomas (W. A. Benjamin, Inc., New York, 1968), p. 337; C. E. Bleil and J. G. Gay, *ibid.*, p. 360.

[4] R. Loudon, Advan. Phys. 13, 423 (1964).

[5] D. A. Kleinman, private communication.

[6] J. L. Birman and A. K. Ganguly, Phys. Rev. Letters 17, 647 (1966); A. K. Ganguly and J. L. Birman, Phys. Rev. 162, 806 (1967).

[7] B. Segall and G. D. Mahan, Phys. Rev. 171, 935 (1968).

[8] If the LO branch has noticeable dispersion, then the multiple-phonon lines due to processes (b) and (c) in Ref. 1 will be much broader than the single-phonon line because the multiple phonons have a distribution of k values. In process (a) only $k \approx 0$ phonons are emitted. Our data show no broadening of the multiple-phonon lines beyond that due to phonon lifetimes, but this does not favor process (a), since there is apparently little dispersion in the LO branch of CdS: Reference 2 gives the frequency of the 2–LO-phonon line as very close to twice that of the one-phonon line.

[9] E. Burstein, D. L. Mills, A. Pinczuk, and S. Ushioda, Phys. Rev. Letters 22, 348 (1969).

EVIDENCE FOR THE EMISSION OF SLOW POSITRONS FROM POLYETHYLENE*

John M. J. Madey
Department of Physics, Stanford University, Stanford, California 94305

(Received 20 December 1968)

A measurable flux of slow positrons was found to be emitted from the surface of a polyethylene absorber.

In 1950, Madansky and Rasetti[1] reported on an attempt to detect thermal positrons which should have, according to their estimates, stood a reasonable chance of being emitted if they started out within a diffusion length of the surface of an absorber. Using positrons from a Cu^{64} source, both metallic and dielectric absorbers were used, but no evidence of slow positron emission was found within the limits of sensitivity of their experiment. However, Cherry,[2] in the course of an experimental determination of the secondary-emission coefficient of positrons, did observe the emission of positrons with energies below 10 eV that had been transmitted through a mica window whose exit side had been coated with a thin film of chromium.

In the case of the dielectric absorbers, it seems likely that the difference in results reflects the preparation of the absorbers used. As is well known in conventional beta spectroscopy, particles stopping or annihilating within dielectric films can charge them to rather high potentials. Some respect for the problem can be gained from estimates of the fields due to annihilating positrons in the absorbers used in this experiment which were in excess of 10^6 V/cm at the interface of the dielectric and the conducting film. Unless at least the exit side of an absorber is maintained at a fixed potential, observation of any slow positron emission is likely to be difficult.

A second aspect of the use of dielectric absorbers is the possibility of field-enhanced emission. An estimate (for polyethylene) of the rate of loss of energy to the acoustic modes for motion parallel to the c axis in a perfect lattice yielded a mean free path of 40 Å and a mobility of 83 cm^2 $(\text{V sec})^{-1}$ for thermal positrons. Assuming a lifetime of 5×10^{-10} sec, the contributions to the rms displacement of a thermalized positron due to diffusion and an applied field would be equal at a field of 10^3 V/cm, amounting to 4400 Å at 300°K. At a field of 10^6 V/cm a drift of 0.44 mm would be predicted. While this number takes no account of the possibility of scattering or trapping by impurities or at crystallite boundaries, it seems likely that a significant enhancement in the number of positrons reaching and penetrating the surface would be expected if a field of this size was actually present.

The spectrometer used in our measurements is shown schematically in Fig. 1. A carrier-free millicurie-level Co^{58} source was electroplated in the form of a ring with a 3-mm i.d. and an 8-mm o.d. on the end of a $\frac{1}{2}$-20NF bolt and mounted a few millimeters behind the dielectric film under test (*D* in Fig. 1). Positrons passing through the dielectric film exit through a metal film deposited on its surface and pass into the spectrometer.

The potential of the metal film and the Co^{58} source to which it was connected could be controlled externally by means of the power supply V_1. Positrons emitted from the film travel down the solenoid through a cylindrical shield *S*, which was maintained at the same potential as the source. A helical groove in the graphite block *H*, maintained at ground potential, allowed only those positrons with the appropriate radius and pitch to pass. A Monte Carlo technique was used to determine the form and magnitude of the resolution function of this "cyclotron state filter."

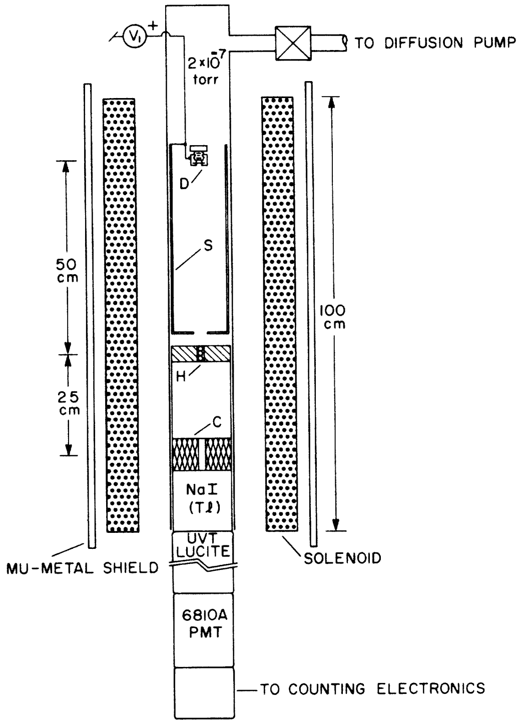

FIG. 1. Positron spectrometer.

By varying the magnetic field and V_1, the desired range of energy could be examined.

Those positrons passing through the filter proceeded through a distance of 25 cm and a lead collimator *C* to annihilate on the face of a NaI(Tl) scintillator. A light pipe carried the resulting light to a phototube outside the field of the solenoid and the pulses, having been shaped, amplified, and selected by height, were totaled in a counter. The detection efficiency, 60% for 2γ annihilations, was measured with a Cs^{137} source which had been calibrated against a National Bureau of Standards' standard.

Counting rates due to slow positrons passing through the filter were at most on the order of 1 sec^{-1}, while the stray radiation due to annihilations above the filter, cosmic rays, and phototube noise accounted for an additional 200 counts/sec. Counts were accumulated for 500 sec at which time V_1 was raised to a positive value high enough to insure that none of the incident positrons could pass through the cyclotron state filter. After another 500 sec of counting in this mode, the difference in counts was taken and accumulated and V_1 returned to its initial value. A flux of slow positrons resulted in a linear increase with time in the accumulated difference. By plotting this difference against time and measuring the slope of the best straight line fit, a usable signal-to-noise ratio could be obtained after 3-4 h of counting. Precautions were taken to minimize externally induced electrical noise and the observed scatter of experimental points in a given run was consistent with that expected on the basis of Poisson statistics.

As in Cherry's experiment a metal film was deposited by evaporation on one side of the absorber. However, our film preparation differed in several respects. We used aluminum instead of chromium. Also, since it seemed likely that the only function served by the film was to establish a potential zero at the surface, and that a substantial number of positrons would otherwise be lost in passage through the metal, the film was deposited in the form of a random grid. Prior to deposition, the dielectric was dusted with 0.3-μ alumina powder. After deposition, the dust was blown off leaving perhaps 50% of the surface free. The metal films were approximately 500 Å thick and, despite the holes, had good conductivity.

The polyethylene was obtained in the form of antioxidant-free homopolymer fluff made by the Phillips process with an estimated impurity level of 200 ppm consisting mainly of silicon and aluminum compounds. The fluff was melted and pressed to the desired thickness in a 10-μ vacuum. Polyethylene whose c axis was preferentially oriented in a plane perpendicular to the surface of the film was produced by the method of Sasaguri, Yamada, and Stein[3] with recrystallization carried out in a dry nitrogen atmosphere. In a well-oriented sample, this technique substantially increases the probability of c-axis alignment within a given angle of the surface normal.

One of the oriented polyethylene samples yielded the spectrum in Fig. 2. Since the spectrometer distinguishes between the energy associated with the cyclotron motion ($E_\perp$) and the linear motion ($E_\parallel$) of the positrons, the flux has the unit of the number of positrons per second per millicurie of Co^{58} per unit area of the $E_\parallel$-$E_\perp$ plane. The spectrometer had a resolution of 2.0 eV in $E_\parallel$ and 0.7 eV in $E_\perp$ (widths included the central 50% of the spectrum passing through the filter).

Although the counting statistics leave something to be desired, application of the χ^2 test to a typical run rules out the alternative interpretation of the data as due to purely random variations in the counting rate. Assuming only random variations, the probability of a linearly increasing accumulated difference corresponding to a datum point lying above 15.5 in Fig. 2 is less than 0.02. The probability of three such adjacent points in a random selection of ten points is less than 6×10^{-5}.

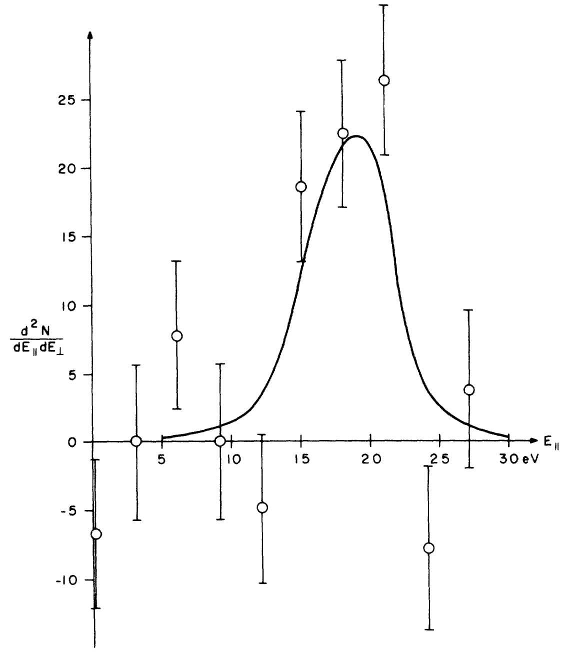

FIG. 2. Spectrum of slow positrons emitted from oriented polyethylene ($E_\perp = 2.3$ eV). The absorber thickness was 0.014 in. The polymer used was Celanese "Fortiflex" with a number average molecular weight of 2.8×10^4 and a density of 0.965. See the text for a definition of the unit of flux.

The smooth curve drawn through the data points represents only an eyeball best fit and, at the very least, is subject to modification as better statistics become available.

Model calculations assuming a perfect lattice indicate that the structure of polyethylene may have a substantial effect on the spectrum of any emitted slow positrons. Based on the available x-ray data[4] and assuming Bloch wave functions for the positrons, the expectation value of the potential for the lowest eigenstate, corresponding to a positron at rest, was found to be +20.7 eV setting a lower limit to the energy of the emitted positrons in rough agreement with the observed value.

Several processes may be operative to limit the positron spectrum at the high-energy end. The presence of excited electronic levels at 10 eV and above makes persistent motion with energy greater than this value unlikely. Also to be considered is positronium formation with a 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.

---

*Work supported by the National Aeronautics and Space Administration under Grant No. NGR-05-020-015.

[1] L. Madansky and F. Rasetti, Phys. Rev. 79, 397 (1950).

[2] W. H. Cherry, dissertation, Princeton University, 1958 (unpublished).

[3] K. Sasaguri, R. Yamada, and R. S. Stein, J. Appl. Phys. 35, 3191 (1964).

[4] C. W. Bunn, Trans. Faraday Soc. 35, 482 (1939).

ELECTRODYNAMICAL BOND-CHARGE CALCULATION OF NONLINEAR OPTICAL SUSCEPTIBILITIES

B. F. Levine
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

(Received 4 March 1969)

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]

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

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

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

where $\frac{3}{4}\sqrt{3}d^{-3}$ 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-