

Emission of Band-Gap-Energy Positrons from Surfaces of LiF, NaF, and Other Ionic Crystals

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(Received 24 August 1984)

Energetic positrons implanted into various ionic crystal surfaces are reemitted with a maximum kinetic energy (14.7 ± 0.7 eV for LiF) near the band-gap energy. The evidence suggests that, at least for LiF and NaF, the emission originates from bulk-formed positronium (Ps) breaking up after diffusing to the surface. In our model, the positrons are Auger emitted when the Ps electrons recombine with holes at the surface, and the spectrum of positron energies thus reflects the density of empty surface states.

PACS numbers: 71.60.+z, 73.20.Cw, 78.70.Bj

It has been known for some time that positrons have a negative affinity for some metal surfaces.¹ After being implanted into these surfaces at high energies, some of the positrons diffuse back to the surface and are ejected into the vacuum with a kinetic energy equal to the negative of the positron work function of the surface, typically a few electron volts. These metal surfaces are presently used as the moderator in many slow-positron-beam devices. It is also known that some insulators, namely² MgO and LiF, also reemit positrons when they are bombarded with kiloelectronvolt energy positrons. In this Letter we report our observation that positron reemission seems to be a general property of the ionic crystals and that the spectrum of the reemitted positrons extends to remarkably large energies. Our experiment sheds light on some old questions concerning the MgO positron moderator³⁻⁵ and gives us new information about the state of positrons in the alkali halides.⁶ The emission mechanism that we propose for the ionic crystals is descended from that of Canter *et al.*³: Ps formed in the solid breaks up at the surface and the positron energy spectrum is proportional to the density of *unoccupied* electron states at the surface. (A similar mechanism for positive muons might prove to be the basis for a μ^+ moderator.) This positron emission process is just the opposite of positronium (Ps) emission from a metal surface, where the Ps velocity distribution is proportional to the density of *filled* electron states at the surface.⁷ The complementarity of Ps breaking up to emit a positron⁸ and a positron grabbing an electron to form Ps is somewhat analogous to that of inverse⁹ and normal photoemission.

Figure 1 displays the differential positron energy spectra we obtained for nine ionic crystal samples. The alkali halide samples were cleaved in air [(100) orientation] and the other samples had polished surfaces. The MgO sample orientation was (100),

the quartz was Z-cut, and the Al_2O_3 had the c axis normal to the surface. The orientation of the CaF_2 is believed to be (110). No other surface preparation was performed except for heating in the ultrahigh vacuum of the experimental chamber ($P = 5 \times 10^{-10}$ Torr). The alkali halide surfaces and the CaF_2 surface exhibited large Bragg maxima for low-energy positron diffraction. While no other surface analysis was performed, the contamination of similarly prepared surfaces is generally less than a monolayer.¹⁰ The spectra were obtained by bombarding the sample surfaces with 500-eV slow positrons from a magnetically guided beam.¹¹ A retarding-field spectrometer measured the axial component of the reemitted-positron kinetic energy. The positrons that passed through the retarding element were $\vec{E} \times \vec{B}$ deflected away from the beam axis and counted directly with a channel-electron-multiplier-array detector. The integral spectra obtained by sweeping the retarding potential were later differentiated, smoothed with a 0.5-eV full width at half maximum Gaussian, and normalized to a common peak amplitude. The total positron yield extrapolated to zero incident positron energy, y_0 , is about 0.4 for each sample. The energy axes in Fig. 1 have been shifted by an amount ΔV that causes the spectra to begin to rise at the zero retarding voltage point. Provided the minimum axial positron energy is zero, ΔV represents the difference between the contact potential of the Mo retarding element and the sample surface, $\Delta V = \phi_{\text{Mo}} - \phi_{-}$. The samples were heated to about 330°C to increase the ionic conductivity and minimize the effects of charging. There is apparently no charging except for the Al_2O_3 and SiO_2 samples.

The main features of the spectra in Fig. 1 are their unique shapes and the large size and great spread of the positron emission energies. The maximum energy is correlated with the magnitude of the electronic band gap indicated by the solid dots

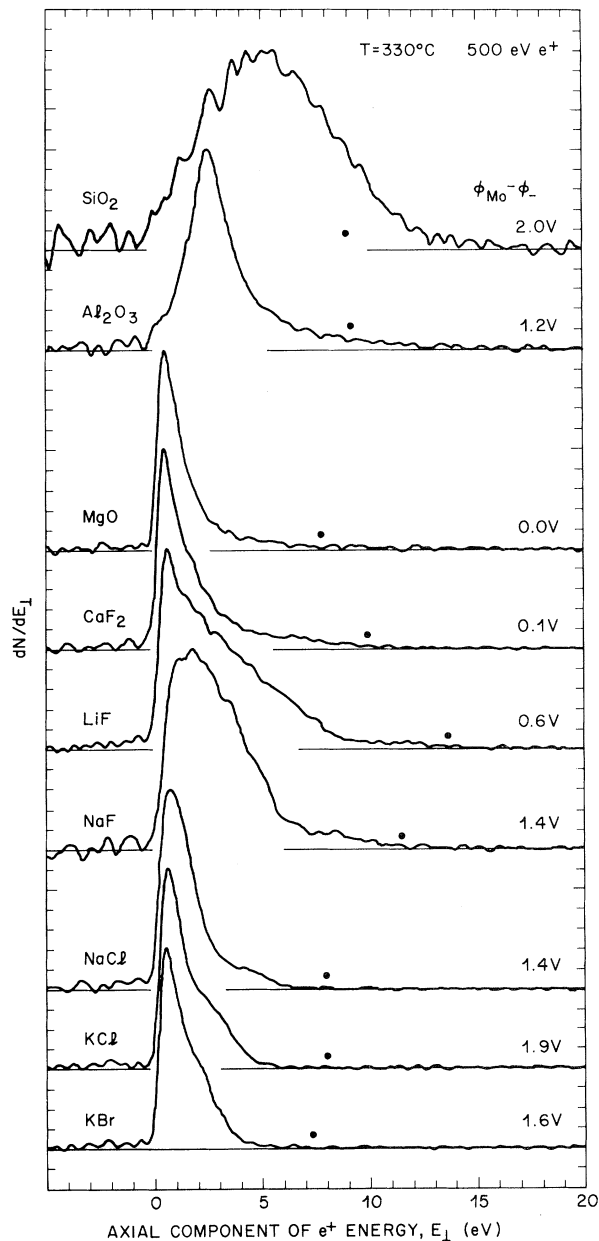


FIG. 1. Positron emission spectra for nine ionic crystal samples.

in the figure. A similar set of data obtained using 1500-eV positrons is (within statistics) identical in shape to the 500-eV data of Fig. 1. We conclude from this that the large energies we observe are not caused by the positrons retaining some of their initial kinetic energy. We have also measured positron-emission energy spectra for a NaF sample that has been tipped by an angle $\theta = 10^\circ, 20^\circ, \dots, 70^\circ$ relative to the beam axis. The curves are all qualitatively the same, although the change in slope seen in Fig. 1 at 6 eV is rounded out for

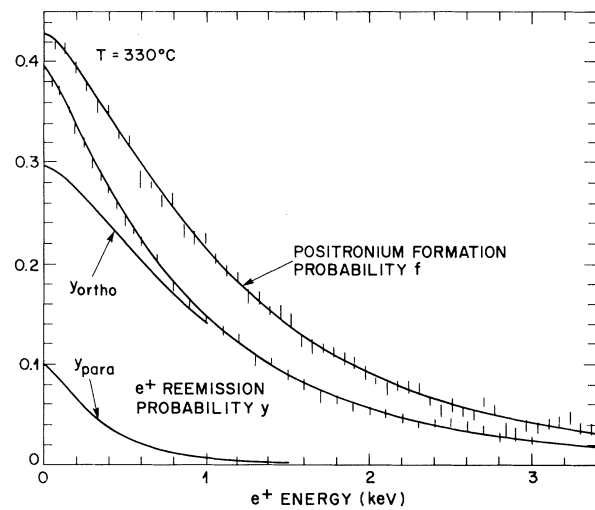


FIG. 2. Energy dependence of the Ps and e^+ yields from NaF.

$\theta > 20^\circ$. Evidently the positron angular distribution is roughly isotropic.

Besides emitting positrons, we find that all the samples studied emit Ps. It is also true that both free positrons and Ps are present in positron-irradiated ionic solids.⁶ Possibly the emitted positrons come from positrons in the bulk, and the Ps from Ps in the bulk. In order to determine whether the Ps and positron emissions have a common origin we have studied the energy dependence of the formation probabilities. Figure 2 shows our measurements on NaF of the negatively-biased-sample Ps yield,¹² f , and the positron yield, y , plotted versus the incident positron energy. Theoretical curves for fitting to the data were generated assuming a positron stopping profile¹³ proportional to $z \exp(-(z/z_0)^2)$, a positron mean penetration depth z_0 proportional¹⁴ to the incident energy E to a power n , and a one-dimensional diffusion model for calculating the probability of the positron returning to the surface. In this model we have (with a similar expression for f)

$$y = y_0 [1 - u \exp(u^2/\pi) \operatorname{erfc}(u/\pi^{1/2})], \quad (1)$$

where $u = z_0(D\tau)^{-1/2}$, and the diffusion length $(D\tau)^{1/2}$ contains the positron diffusion constant D and the mean lifetime τ of the diffusing species. Experimentally,¹⁵ the median penetration depth is $z_{1/2} = aE^n/\rho$, where $n = 1.6 \pm 0.1$, $a = 3.3 \pm 0.8 \mu\text{g}/\text{cm}^2$ for E in kiloelectronvolts, and ρ is the density. Using $z_0 = (\pi/\ln 16)^{1/2} z_{1/2}$, we may write $u = (E/E_0)^n$, where $E_0^{2n} = D\tau\rho^2 \ln 16\pi^{-1} a^{-2}$.

The Ps yield data are fitted well by Eq. (1) with $f_0 = 0.43(3)$, $E_0 = 1217(13)$ eV, $n = 1.37(3)$, and $\chi^2/\nu = 100.5/97$. The positron yield data are fitted

by Eq. (1) with $y_0 = 0.398(2)$, $E_0 = 883(8)$, $n = 1.21(1)$, and $\chi^2/\nu = 73.2/37$. If we fit the latter data using two components to correspond to the different diffusion lengths of para and ortho Ps in the solid, and fix the relative amplitudes of the two components at 0.25 and 0.75, we find $y_0 = 0.395(3)$, $E_0^p = 359(33)$, $E_0^o = 1145(21)$, $n = 1.42(4)$, and $\chi^2/\nu = 59.9/36$. The chi square per degree of freedom of the two-component fit is much improved and the E_0^o value is nearly the same as the E_0 determined from the Ps yield data. Note that since para Ps decays via 2γ 's whether or not it escapes from the solid, the Ps yield versus energy measurement is only sensitive to the ortho-Ps diffusion. The total amount of Ps formed in the bulk implied by the two-component fit is $y_0 + (1 - y_0)f_0 = 0.62(2)$. This is consistent with the measurement of Hyodo and Stewart¹⁶ if we assign their entire long-lifetime component of intensity 0.47(1) to ortho Ps to get a Ps fraction $(4/3)0.47(1) = 0.63(1)$. Although the intensities are in good agreement, the ratio $E_0^o/E_0^p = 3.2$ is too large when compared to the lifetime¹⁶ ratio raised to the $1/(2n)$ power. The positron yield data for LiF also suggest a two-component diffusion, but most of the other samples are adequately fit by a single component. Further study is required on these other samples.

Another piece of information comes from our positron diffraction measurements which will be presented elsewhere. For all the samples except the three oxides we observe a series of Bragg peaks, the locations of which can be explained by a positron inner potential and a slightly relaxed lattice constant. The inner potentials for LiF and NaF are +0.7 and -0.5 eV which implies that the positron work functions are $\phi_+ = -0.7$ and +0.5 eV, respectively. Probably the sharp portions of the emission spectra at low energies for LiF and CaF₂ (the two samples for which ϕ_+ is negative) are due to a small-intensity direct-positron-emission component. It would be consistent with the measurements of Ref. 5 if the low-energy portion of the positrons from MgO were also emitted via a negative work function; unfortunately, we did not observe any Bragg peaks for this sample.

It thus appears that at least for LiF and NaF we may attribute the Ps and positron emission primarily to the diffusion of Ps to the surface. The diffusion constants D deduced from E_0 [$D = 0.008(4)$ and $0.0010(5)$ for NaF and KCl] are much smaller than we find for positrons in metals.¹⁵ This suggests¹⁷ that the diffusing state could indeed be the self-trapped Ps state of Hyodo, Kasai, and Takakusa.¹⁸ Canter *et al.*³ suggested that Ps could be field

ionized when leaving a surface. We would suggest rather that the positron is Auger emitted when the electron falls into an empty surface state. This hypothesis leads to estimates of the maximum positron emission energy (see Fig. 3) in accord with the observations. For example, the Ps binding energy¹⁹ in NaF is 3.2(2) eV, the energy gap²⁰ is $E_g = 11.5$ eV, and the width of the valence band²¹ is $\Delta E_v = 4.0(5)$ eV. The maximum positron energy E_{\max} in the process $\text{Ps} \rightarrow e^+ + e^-$, assuming the e^- finds a hole at the bottom of the valence band, is then

$$E_{\max} = E_g + \Delta E_v - E_b - \phi_+ = 11.8(6) \text{ eV}, \quad (2)$$

in good agreement with the maximum energy measured in Fig. 1.

One possible difficulty with our model is the necessity of there being empty states in the band gap at the surface. A photoemission experiment²¹ on air-cleaved NaF shows that there are some filled surface states in the gap. An inverse photoemission experiment could tell us about any empty states. Empty states below E_f (located²¹ about 4.5 eV below the bottom of the conduction band for air-cleaved NaF at 300°C) would not ordinarily be present. However, the energetic positron leaves a trail of electron-hole pairs. Possibly some of the holes diffuse to the surface and survive long enough to cause the breakup of the Ps.

We have presented evidence indicating that the

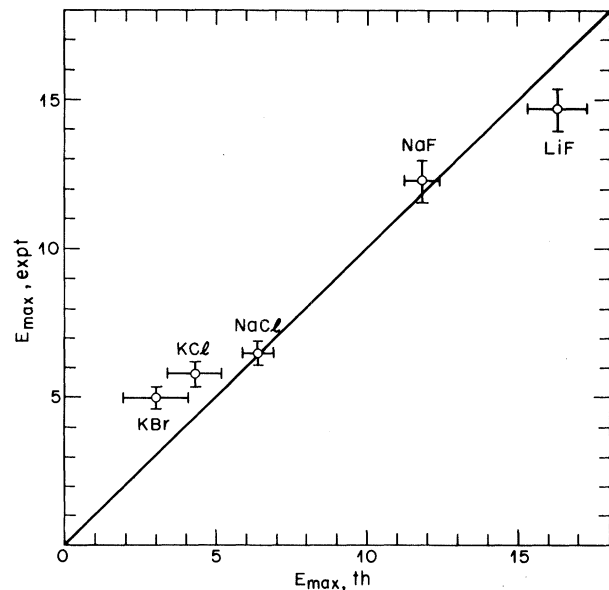


FIG. 3. Comparison of the theoretical [from Eq. (2)] and experimental (from Fig. 1) maximum positron emission energies for the five alkali halide samples.

large-energy positron emission from LiF and NaF is caused by Ps breakup. If our picture of the Auger emission mechanism is correct, the spectrum of positron energies should reflect the density of empty electron states. It would be interesting to study the positron emission in the presence of adsorbates as a further test of this model. It would also be informative (1) to study surfaces cleaved in vacuum to see if the surface states are associated with the ideal surface; (2) to make measurements at low temperature to see if the Ps Bloch state¹⁸ has a large diffusion constant; (3) to extend the measurements to the rare-gas solids, in particular Ne which has a 22-eV band gap²⁰; and (4) to see if protons and positive muons are also emitted by the large-band-gap solids.

The authors would like to thank S. Berko, W. L. Brown, J. H. Brewer, K. F. Canter, A. Dupasquier, D. R. Harshman, S. D. Kevan, K. G. Lynn, C. J. Oram, P. M. Platzman, and N. V. Smith for valuable discussions.

Note added.—We have recently found that the vacuum-cleaved surfaces of NaF and LiF have positron emission spectra very similar to the ones shown in Fig. 1.

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