Evidence for Quasi Two-Dimensional Positronium Formation in Potassium-Intercalated Graphite

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Two-dimensional angular correlation of annihilation radiation (2D ACAR) experiments have been performed to study the electron-positron momentum densities in potassium-intercalated graphite and in highly oriented pyrolytic graphite. Magnetic-field–dependent experiments indicate that the high-intensity, anisotropic 2D ACAR component observed in $C_{24}K$ is at least partially due to quasi-2D positronium formation. In the highly oriented pyrolytic graphite 2D ACAR spectra, a low-intensity, nearly isotropic, thermally activated positronium component is found.

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Graphite-intercalation compounds (GIC's) have been the subject of extensive experimental and theoretical studies.[1] Alkali-metal intercalates (AGIC's) exhibit a rich variety of quasi two-dimensional (2D) phenomena; however, details of their electronic structure, such as charge transfer and the nature of the interlayer band, are still not fully clarified. Positron (e^+) annihilation experiments,[2] using the technique of angular correlation of annihilation radiation (ACAR),[3] can yield the momentum density of the electrons (e^-) sampled by the thermalized e^+; in metals ACAR spectra exhibit discontinuities that map out the Fermi surface (FS). In some insulators, however, the e^+ forms positronium (Ps), yielding narrow ACAR components that reflect the motion of the Ps atom. In a series of papers, Cartier *et al.*[4] reported e^+ data from various GIC's, using "long-slit" geometry that yields the 1D projection of the e^--e^+ momentum density (1D ACAR). In most AGIC's they observe an anisotropic, high-intensity momentum component with its narrow dimension along the carbon planes, and interpret this as e^+ annihilation with a nearly free, low-density 2D e^- gas.[4]

In this Letter we present evidence that at least part of the anisotropic component in stage-two potassium-intercalated graphite ($C_{24}K$) is due to e^+ annihilation from a quasi-2D Ps state rather than from direct annihilation with conduction electrons, thus casting some doubt on the FS interpretation of Cartier *et al.*[4] Our evidence is based on magnetic-field–dependent measurements using the more sensitive[3] "point-slit" geometry that yields 2D projections of the e^--e^+ momentum density (2D ACAR).[3] For comparison, we also have studied 2D ACAR spectra in samples of highly oriented pyrolytic graphite (HOPG).[1] We observe a narrow, thermally activated component which we also assign to Ps formation; the Ps component in HOPG, however, is more isotropic and far less intense than in $C_{24}K$. The discovery of nearly 2D Ps formation in $C_{24}K$ opens the possibility of many new e^+ and Ps experiments in layered compounds, and challenges theoretical modeling involving 2D Ps interactions with low-density conduction electrons.

The 2D ACAR experiments have been performed with the 32×32 NaI(Tl) multidetector system described earlier.[5] The spectra were obtained on a 0.4×0.4-mrad^2 mesh [1 mrad$\cong mc\times(10^{-3}$ momentum units)], with a set of 1.5- or 0.75-cm-diam Pb collimators, and a 10-m detector-to-sample distance. ^{58}Co e^+ sources of up to 500 mCi were used, placed 1 cm from the sample between the pole faces of a 23-kG magnet. The samples were mounted on a variable-temperature copper stage, in a 10^{-6}-Torr vacuum. The AGIC samples were prepared from 6×8-mm^2 slabs of HOPG cleaved to $\simeq1$ mm thickness. They were transferred rapidly via a dry-argon–filled plastic bag into the sample chamber, which was then evacuated. The stage of the intercalates was identified by color. The normal to the sample surfaces was along the c axis; as in HOPG, the crystallites are randomly oriented in their basal plane.[1]

The 2D ACAR spectrum represents the projection $N(p_\parallel,p_\perp)=\int\rho^{2\gamma}(\mathbf{p})dp'_\perp$ of $\rho^{2\gamma}(\mathbf{p})$, the 3D momentum density of the e^--e^+ pair, where $p_\perp$ ($p_\parallel$) is $\perp$ ($\parallel$) to the c axis, and $\mathbf{p}'_\perp$ is along a line joining the detectors and the sample ($\mathbf{p}'_\perp\times\mathbf{p}_\perp=\mathbf{p}_\parallel$). In Figs. 1(a) and 2 (top) we plot the spectrum for HOPG at 100 K, in perspective and in contour-line form, for better visualization. The distribution is bimodal with a saddle point at $(p_\parallel, p_\perp)=(0,0)$. The large anisotropy was observed a long time ago in a 1D ACAR experiment[6]; the lobes were explained in terms of a delocalized interlayer e^+ sampling preferentially the π electrons. The projection of the graphite Brillouin zone onto the $(p_\parallel,p_\perp)$ plane leads to lines 3.6 mrad apart, corresponding to the hexagonal faces; the faces parallel to c are rotated randomly in HOPG, between $p_\perp=5.70$ mrad (ΓM) and $p_\perp=6.58$ mrad (ΓK). We see from Fig. 2 (top) that the thermalized e^+ samples electrons with momentum amplitudes in several zones along the c direction; in the $p_\perp$ direction, however, their amplitude decreases rapidly outside the first zone indicating nearly free-electron behavior along the carbon planes.[7] The FS of graphite encloses too small a volume to be detectable in our 2D ACAR spectrum.

The e^--e^+ momentum density changes drastically upon intercalation. Figures 1(b) and 2 (bottom) show

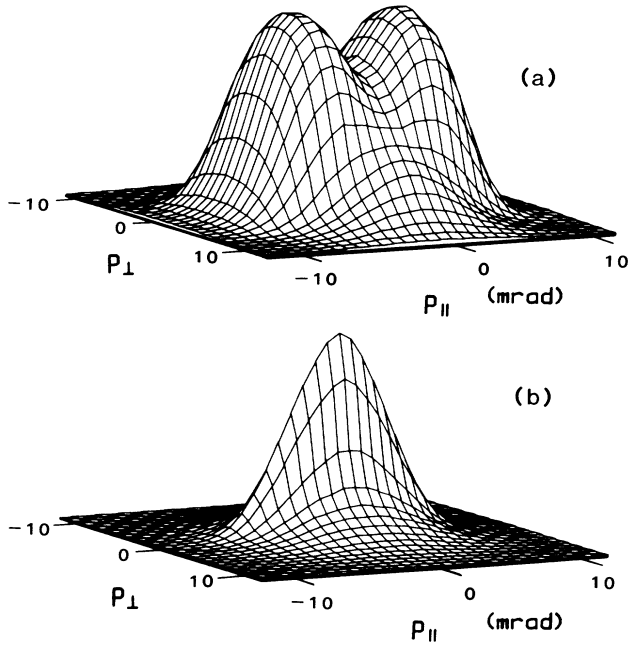

FIG. 1. 2D ACAR spectra for (a) HOPG and (b) $C_{24}K$, at 100 K. Momenta ∥ (⊥) to the c axis, $p_{\parallel}$ ($p_{\perp}$), in units of mrad$\cong mc\times10^{-3}$. The 2D resolution is nearly a 2D Gaussian of FWHM$\simeq$1.4 mrad. For clarity, lines are drawn only every 0.8 mrad, while data were taken every 0.4 mrad. The data are not symmetrized in either direction.

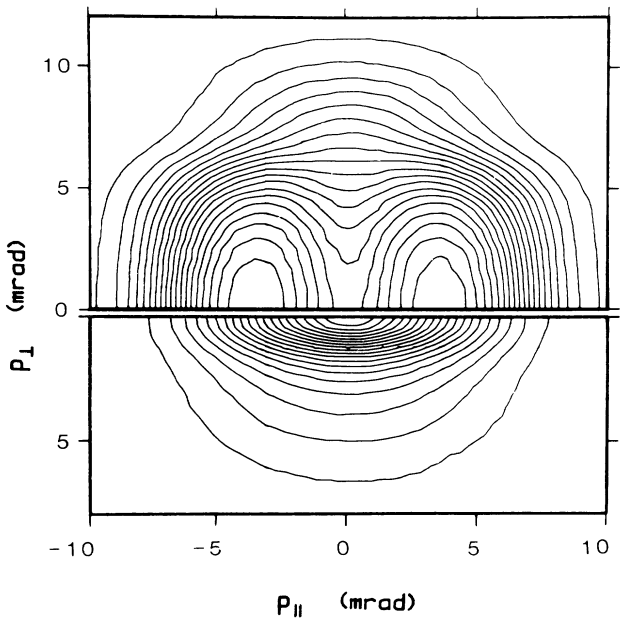

FIG. 2. Contour-line representation of half the 2D ACAR spectra of Fig. 1, for HOPG (top) and $C_{24}K$ (bottom). Momenta ∥ (⊥) to the c axis, $p_{\parallel}$ ($p_{\perp}$), in units of mrad$\cong mc\times10^{-3}$. Contours are equally spaced, in steps of 5%, from 5% to 95% of peak height for each sample.

$N(p_{\parallel},p_{\perp})$ for a $C_{24}K$ sample at 100 K. We observe a highly anisotropic, 2D "tongue"-shaped surface superimposed on a broad, nearly isotropic distribution [the two 1D ACAR curves in Ref. 4 correspond to the integrals of $N(p_{\parallel},p_{\perp})$ along $p_{\perp}$ or $p_{\parallel}$]. The broad distribution can be fitted by an isotropic 2D Gaussian with a full width at half maximum (FWHM) of 11.2 ± 0.2 mrad of (28 ± 1)% intensity, and a second, 2D Gaussian with a FWHM of 7.1 ± 0.2 mrad along $p_{\perp}$ with an 11% elongation along $p_{\parallel}$, and a (39 ± 1)% intensity.[8] Subtraction leaves a (33 ± 2)%-intensity anisotropic tongue with a FWHM$_{\perp}$ of 1.76 ± 0.5 mrad along $p_{\perp}$ and a FWHM$_{\parallel}$ of 7.26 ± 0.05 mrad along $p_{\parallel}$. The FWHM values above are after deconvolution by our 2D angular resolution. Independent scans with the 0.75-cm collimators agree with these results, which were taken with the 1.5-cm collimators. At 295 K we observe an increase in tongue intensity[9] to (42 ± 2)%, with a FWHM$_{\perp}$ of 2.36 ± 0.05 mrad and a FWHM$_{\parallel}$ of 7.08 ± 0.05 mrad. We also obtained a similar 2D ACAR spectrum in a stage-one (C_8K) sample, albeit with lower statistics.

Cartier *et al.*[4] analyze the narrow component of their 1D ACAR spectra in terms of an inverted parabola, corresponding to a nearly free-electron FS centered about the Γ point ($\mathbf{p}=0$). An analysis of the cross section of our 2D tongue does not seem to support such a picture: A single inverted ellipse[3] (corresponding to the inverted parabola in 1D geometry), convoluted with our resolution, cuts off too sharply to be an acceptable fit along $p_{\perp}$. In addition, Cartier *et al.*[4] assign the high-momentum components of their 1D ACAR data to annihilation with graphitic electrons. A comparison between our HOPG and $C_{24}K$ 2D ACAR spectra shows a substantial difference at high momenta. The e^+ wave function appears to be quite different in the intercalates than in pure HOPG.

We were thus led to question the origin of the anisotropic ACAR component and performed magnetic quenching and polarization experiments, to test for possible Ps formation. In the presence of a magnetic field $\mathbf{B}$, the spin states of Ps are mixed,[10] leading to an increase in the direct 2γ annihilations from the singlet state (producing a narrow ACAR component), and a decrease (quenching) in the broad ACAR component because of triplet-state 2γ annihilations with the non-Ps electrons (the "pickoff" process).[2] In addition, a spin-aligned e^+ (due to parity nonconservation in β^+ decay) exhibits a "polarization" effect, leading to an increase in singlet formation when the field $\mathbf{B}$ points along ($\uparrow$) the e^+ spin.[11] These effects are specific to Ps, as distinct from direct annihilation without Ps formation.[12] In a 2D ACAR experiment the polarization effect is simpler to interpret, since in a quenching experiment the e^+ beam diameter depends on $|\mathbf{B}|$, leading to a $|\mathbf{B}|$-dependent

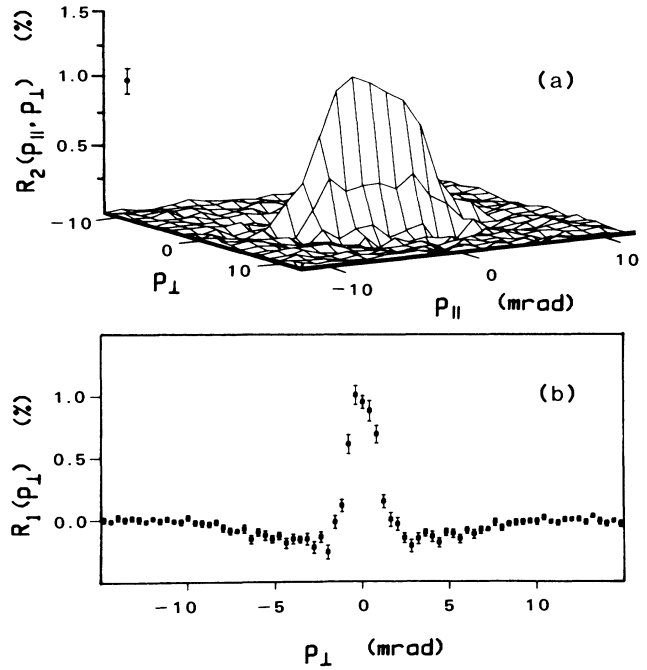

FIG. 3. Polarization effect for $C_{24}K$ at 100 K as discussed in the text; (a) is obtained from 2D ACAR data, while (b) is the 1D equivalent. Momenta $\parallel$ ($\perp$) to the c axis, $p_\parallel$ ($p_\perp$), in units of mrad $\cong mc\times 10^{-3}$. The statistical uncertainty of the $p_\parallel=0$, $p_\perp=0$ point is shown on the left of (a).

effective $p_\perp$ resolution that complicates the analysis. We have performed a high-precision polarization experiment (1.4×10^7 counts per spectrum) on the $C_{24}K$ sample at 100 K, by reversing the direction of the 23-kG field periodically ($\uparrow$ or $\downarrow$). The observed effect is shown in Fig. 3(a) as

$$R_2(p_\parallel,p_\perp)=[N_\uparrow(p_\parallel,p_\perp)-N_\downarrow(p_\parallel,p_\perp)]\times[N_\uparrow(0,0)+N_\downarrow(0,0)]^{-1}.$$

We note that, within statistics, $R_2(p_\parallel,p_\perp)$ has the shape of the 2D anisotropic tongue, thus proving conclusively that at least part of the tongue is due to Ps formation. The increase in the tongue region is compensated by a decrease at high momenta. This effect is seen more clearly by our forming $R_1(p_\perp)=\int R_2(p_\parallel,p_\perp)dp_\parallel$, as plotted in Fig. 3(b). We also performed a less precise quenching experiment by lowering $|\mathbf{B}|$ to 5.75 kG, and obtained a decrease of the tongue intensity by $\sim 18\%$. The quenching and polarization effects versus $|\mathbf{B}|$ depend in a complex way on the pickoff rate, a possible Ps singlet-triplet spin-exchange rate, and the e^+ polarization, as well as the effective size of the quasi Ps in the solid.[13] More data at various fields, as well as lifetime data, will be needed to determine these parameters uniquely.

To test for possible Ps formation in HOPG we measured the temperature (T) dependence of the 2D ACAR spectra. Besides observing a slight shrinking of the spectrum along $p_\parallel$ due to the anisotropic thermal expansion of HOPG, we find a distinct, additional filling in of the (0,0) saddle point with increasing T. Differences in spectra between 100 K and higher T show a narrow ($\simeq$2-mrad FWHM), nearly isotropic, low-intensity component centered at (0,0), that reaches an intensity of $(0.30\pm 0.05)\%$ of the 2D ACAR volume at 850 K. We assign this component to thermally activated Ps formation[14] at the surface, as well as at possible "internal surfaces." From its T dependence we obtain an activation energy of 0.20 ± 0.05 eV.[15] Low-energy e^+ beam experiments are presently being performed on HOPG surfaces to study surface Ps formation in more detail.[16] Clearly the Ps in HOPG is of a different nature than in $C_{24}K$.

One can speculate about the nature of the Ps revealed in the potassium intercalate. The shape of the momentum density in $C_{24}K$ indicates a highly anisotropic center-of-mass Ps wave function. The $FWHM_\parallel$ of the tongue component leads, by a simple uncertainty argument, to a Ps spatial distribution confined to a few angstroms along the c axis. The $FWHM_\perp$ is broader than expected for a free Ps at 100 K; a characteristic confinement size would be an order of magnitude larger than along the c axis. A possible locus of such Ps could be in anisotropic microvoids[17] of similar size; given the large intensity of the tongue, however, we seek possible alternative explanations. In ordinary metals Ps cannot form because of the high density of conduction electrons[18]; in K intercalates, however, the conduction electrons at the alkali layer might be of sufficiently low density for Ps to exist. A preliminary 2D ACAR experiment on C_8Cs at 100 K yields a 15% smaller tongue $FWHM_\parallel$ than in $C_{24}K$, reflecting perhaps the larger C-Cs-C layer distance[1] (5.94 Å) than the C-K-C distance[1] (5.39 Å). This effect supports the picture of the Ps atom residing around the alkali-metal layer, if Ps is also responsible for the tongue in C_8Cs. We have also performed a polarization experiment on the $C_{24}K$ sample at 295 K, with the same precision as at 100 K, and obtain, within statistics, a null effect. This can still be consistent with the existence of Ps, if a large spin-exchange rate is present.[13] In AGIC's such a spin exchange can be due to Ps–conduction-electron interactions. Thus the simultaneous decrease in the polarization effect with the increase in tongue intensity could be due to a strong increase in spin-exchange interactions at 295 K. Given the complex structural transitions taking place in $C_{24}K$ between 100 and 295 K,[1] the Ps wave function can undergo substantial spatial changes, leading perhaps to the observed effects. The temperature dependence of the e^+ lifetime will be a most valuable test of this picture.

We are extending our temperature and magnetic-field–dependent 2D ACAR experiments to other stages

of K intercalates as well as to other GIC's; lifetime experiments will also be performed. Should Ps formation occur in all stages where the narrow momentum component appears,[4] a more quantitative model describing thermalized e^+ behavior and Ps formation can emerge. Since Cartier *et al.* have found that the intensity of the narrow momentum component does not have a simple stage dependence,[4] such a model could require a stage-dependent e^+ trapping picture similar to that proposed by them.[9]

In summary, we have studied the electron-positron momentum densities in HOPG and $C_{24}K$ by the 2D ACAR technique, and have presented evidence for a 2D positronium state in $C_{24}K$.

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