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Positron Annihilation in Graphite Intercalation Compounds

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Graphite intercalation compounds have been studied by positron annihilation experiments. In donor compounds, a highly inhomogeneous charge distribution is detected by Coulomb repulsion of the positrons from the intercalant. In acceptor compounds, however, quasifree positron-anion systems are formed within the intercalant. This is used to identify the anionic species.

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Graphite intercalation compounds (GIC's) have been studied for more than fifty years.[1] It is known that they form ordered sequences of graphite and intercalated layers.[2] In many cases, they exist in different "stages," where the stage n is determined by the number of carbon planes between two successive intercalated layers. In the past few years, GIC's have attracted increased interest because of possible applications in electrical conduction, catalysis, electrochemical systems, and other fields.[3,4] Simultaneously, scientific interest has been stimulated, particularly in the field of electronic properties of these compounds.[3,4] One area of interest concerns the local charge distribution in GIC's. Whereas earlier experiments were interpreted by a homogeneous charge distribution,[5] recently Pietronero *et al.*[6] have shown theoretically that the intercalant layer is screened nonhomogeneously according to a power law. The experiments which have been carried out so far have only revealed a distinction between the bounding graphite layers next to the intercalant and the other interior graphite layers.[7-9] Another area of interest deals with the identification of the intercalant species within the graphite sublattice. In particular, the location and the amount of charge in the intercalant layers have been subject to discussions.[10-15]

In the present paper we report the first results of positron annihilation experiments obtained with donor- and acceptor-intercalated graphite. The effects are much larger than those normally encountered with use of the positron as a solid-state probe and there is a pronounced difference between the behavior of donor and acceptor compounds. The probability for an annihilation process with a pair momentum p_z perpendicular to the quanta emission is described by the 2γ angular correlation distribution (ACD), $N(\theta)$, where $\theta = p_z/m_0c$. The quantity $N(\theta)$ depends on the Fourier transform of the electron-positron wave-function product.[16] In most applications of ACD, the primary aim is to investigate the electronic structure of solids. In many cases it is sufficient to approximate the positron wave function by a plane wave with wave vector $k_+ \simeq 0$. In the present experiments, however, the surprisingly pro-

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nounced distortion of the positron wave function, caused by the intercalant layers in GIC's, is used to investigate the charge distribution in donor GIC's and to identify the anionic species in the intercalant layer of acceptor GIC's. Thus significant contributions to the above-mentioned problems can be made.

The 2γ angular correlation distributions were measured with a conventional long-slit spectrometer[17] at an angular resolution of 0.5 mrad (full width at half maximum). The positron sources were produced by neutron irradiation of 30-μm copper foils. The activity was 600 mCi at the beginning of the measurements. In order to avoid oxidation, the samples were introduced into the spectrometer chamber under dry argon atmosphere. All measurements were carried out at room temperature under a pressure of 10^{-6} mbar. For all samples the starting material was highly oriented pyrolytic graphite (HOPG). Most samples were grown by the classical two-temperature technique in Pyrex vessels.[18] Samples with high stage number ($n > 5$) were prepared by decomposition of more concentrated GIC's. The stage numbers were determined by x-ray ($00l$)-reflection analysis. Only samples of a pure stage with narrow x-ray lines were used in the measurements.[19] Some samples were subjected to another x-ray analysis after the annihilation experiments to ensure that no changes occurred during the measurements.

Earlier measurements of the ACD in pure graphite were made on natural monocrystals[20] and on samples prepared by pressing graphite flakes.[21] In order to characterize the starting material HOPG used in this investigation the ACD's were measured with the crystallographic c axis parallel (Fig. 1) and perpendicular to p_z. The results agree well with the earlier measurements mentioned above. In the first orientation, two maxima appear at ±3 mrad which are due to the π-electron contribution to the ACD.[20] The ACD with $c \perp p_z$ is bell-shaped. The unusual central minimum in the orientation $p_z \parallel c$ is very helpful for the discussion of the present experiments.

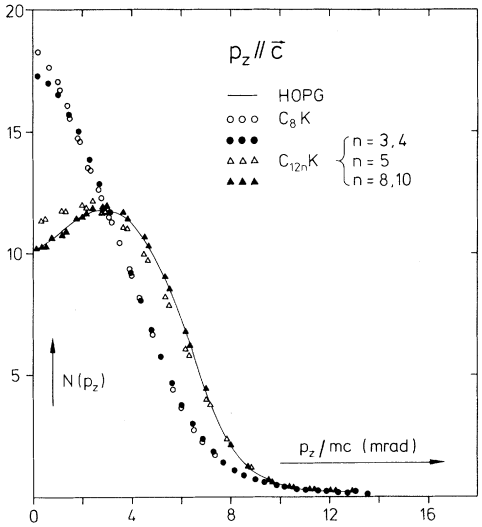

FIG. 1. 2γ angular correlation distribution of HOPG and potassium-intercalated graphite at different stages. γ emission is perpendicular to the crystallographic c axis. All curves are normalized to equal area.

The results ($c \parallel p_z$) for potassium *(donor)-intercalated graphite* at different stages n are shown together with the ACD of pure HOPG in Fig. 1. The ACD's of the compounds with $n = 10$ and 8 are practically indistinguishable from that of the pristine HOPG. Even at $n = 5$ the central minimum typical for HOPG is preserved. Between $n = 5$ and $n = 4$, however, a dramatic change occurs: The ACD jumps into a central-peak structure. This peak becomes sharper with further decrease in n. The similarity of the higher-stage compounds ($n > 5$) with pure graphite clearly shows that the positron annihilation takes place predominantly in undisturbed graphitic regions. This is certainly due to the Coulomb repulsion of the positron from the positively charged donor layers forcing the positron to sample regions far enough from the intercalant layers. The obvious fact that this behavior completely disappears at $n = 4$ suggests that the electronic distortion introduced by the potassium intercalant extends over two neighboring graphite layers. The distance between the basal planes of graphite, d_C, is 3.35 Å. The potassium intercalant expands the distance between C layers adjacent on both sides of the K layer to $d_C + d_i = 3.35 + 2.05$ Å. A rough estimate of the screening length in stage-4 donor compounds yields $\lambda_s{}^+ \equiv \frac{1}{2}d_i + \frac{3}{2}d_C \simeq 6$ Å. This result is consistent with the theoretical concept of Pietronero *et al.*[6] The shape of the ACD of $n \leq 4$ GIC's (Fig. 1) might suggest the existence of voidlike defects.[22] That this does not apply is shown by lifetime measurements. In a stage-1 GIC, a one-component spectrum with $\tau = 306$ psec is observed. This is much smaller than the values of ~500 psec typical for positron trapping in voids.[23] In this context, it is important to notice that the higher-stage compounds were produced by deintercalation of the lower-stage ones.

The sudden change of the ACD observed between $n=4$ and $n=5$ can hardly be attributed to positron-trapping sites produced during the intercalation reaction, since the ACD's of stage 8 and 10 GIC's are indistinguishable from that of the pristine HOPG.

Figure 2 shows the experimental correlation function ($c \parallel p_z$) obtained with $SbCl_5$*(acceptor)-intercalated graphite* at stages $n=2$ and 7 and with a very dilute $SbCl_5$ compound. The latter is characterized by a purely graphitic x-ray pattern, which confirms that the dilution is $<1\%$. The nature of the intercalant species is not well known. Possibly, the composition of the intercalant is partly due to the oxidation reaction $3SbCl_5 + 2e \rightarrow SbCl_3 + 2SbCl_6^-$, in analogy to reaction schemes proposed for group-V fluoride compounds.[12,14,24,25] In sharp contrast to the donor compounds, the ACD is independent of the stage number n here. Furthermore, the distribution shows a bell shape, which is completely different from that of pure graphite. This difference can be explained by a very strong attraction of the positron by the anionic species in the acceptor intercalant, preventing positron annihilation in the graphitic regions of the sample even at very low anion concentrations. The fact that the shape of the ACD is completely independent of the intercalant concentration seems to be a strong argument for the formation of a bound state between the positron and the anions (X^-). Farazdel and Cade[26] calculated theoretical ACD's for free positronium halides $[X^-; e^+]$. As shown by these authors, a comparison of the theoretical results with experimental data is not possible in the case of alkali halides. A fairly large free volume is necessary for the undisturbed annihilation of these complexes. This condition is satisfied for aqueous solutions of alkali halides[27] and also for acceptor GIC's, since the distance between the carbon layers adjoining the intercalant is as large as 8 Å.[28] In fact, the comparison of the data obtained with stage-2 $SbCl_5$- and ICl-intercalated graphite compounds with the theoretical curves[26] for different positronium halides (Fig. 3) heavily supports the assumption that the ACD characteristics in acceptor GIC's are governed by the annihilation of nearly free $[X^-; e^+]$. There is an excellent agreement between the experimental data obtained with ICl-intercalated compounds and the system $[Cl^-; e^+]$. Apparently, the iodine content in the intercalant does not contribute to the experimental results, which suggests that iodine remains unoxidized, probably because of its lower electronegativity. This explanation is supported by the observation that in IBr-intercalated graphite the positronium bromide $[Br^-; e^+]$ is the predominant annihilation center. The ACD's obtained with $SbCl_5$-intercalated graphite compounds are slightly narrower than those of the ICl-inter-

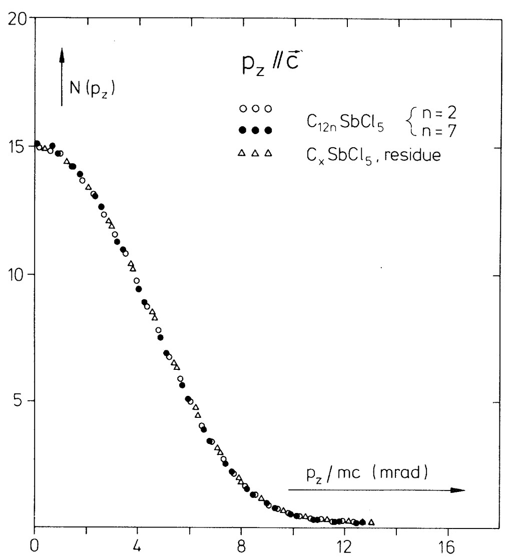

FIG. 2. As in Fig. 1: $n=2$, 7, and very dilute $SbCl_5$-intercalated graphite.

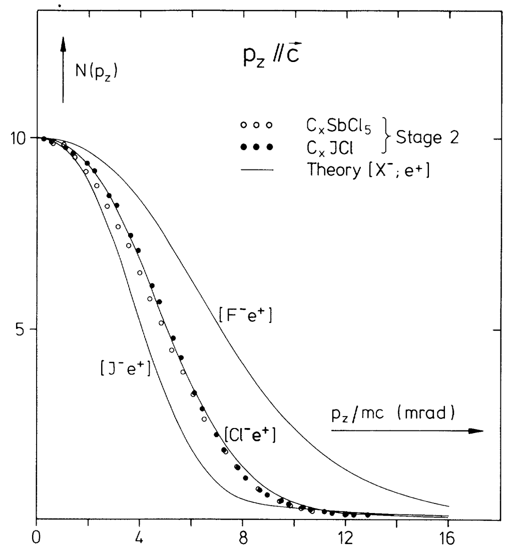

FIG. 3. Comparison of stage-2 $SbCl_5$- and ICl-intercalated graphite with theoretical angular distributions, calculated for the ground state of positronium halides by Farazdel and Cade (Ref. 26).

calated graphite compounds, which might be due to the formation of complex ions during intercalation. All these observations suggest a method of identifying the anionic species within the intercalant. For the ICl and IBr intercalated graphite compounds the anions responsible for positron trapping are certainly Cl$^-$ and Br$^-$, respectively; with SbCl$_5$, the trapping site might be the complex ion SbCl$_6^-$. From the fact that the observed ACD's are independent of the intercalant concentration, another important conclusion can be drawn: In contrast to donor GIC's, the ionization state of the ions within the acceptor intercalant seems to be independent of the intercalant concentration.

In summary, the following conclusions can be drawn: In donor GIC's, positrons are forced to sample the carbon layers of the specimen. Therefore, positrons are very sensitive probes for studies of the charge distribution in these layered materials. In acceptor GIC's, however, positrons are localized in the intercalant layer forming nearly free positron-anion complexes. Therefore, positrons are a powerful tool for the identification of the anionic species within the intercalant.

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