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Angular Correlation of Annihilation Photons in Ice Single Crystals

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Linear-slit angular-correlation curves were obtained at − 148 °C for the [0001], [10$\bar{1}$0], and [11$\bar{2}$0] directions in single crystals of ice. Besides the narrow central peak, pronounced narrow side peaks were also observed. They occurred at angles $\theta = 2\pi\hbar g_z/mc$, where g_z is the projection of reciprocal-lattice vectors $\vec{g}$ on the direction perpendicular to the slits and the sample surface. The relative area of the central plus the side peaks was $(15.2 \pm 0.4)\%$ for all curves. All the peaks are interpreted as due to parapositronium annihilation. The side peaks are explained as evidence for the positronium center-of-mass wave function being a Bloch function, i.e., that positronium is delocalized in ice.

We would like to give a preliminary report on measurements of angular correlation of annihilation photons in single crystals of ice. We used a standard linear-slit angular-correlation setup. The detectors covered a solid angle of about 0.48× 178 mrad as seen from the sample, and we used an external source of 25-mCi $Na^{22}Cl$. The ice single crystals were grown at a rate of 10^{-4} cm/sec by a modified Bridgman method using triple-distilled water. They were then zone-refined once. Since the growing was not done under vacuum, an equilibrium concentration of air molecules (N_2, O_2, CO_2, Ar, etc.) was always present in the liquid phase. The sample temperature was − 148 °C. During the measurements the crystals were contained in an evacuated chamber with a 1-mm-Hg pressure.

The angular-correlation curves for the crystal directions [0001], [11$\bar{2}$0], and [10$\bar{1}$0] along the z direction (i.e., the direction perpendicular to the slits and the sample surface) are shown in Fig. 1. The curves are symmetric around $\theta = 0$. Figure 2 shows parts of the curves obtained by use of 0.24-mrad slit width. In Fig. 2 the broad component is approximated by the shown Gaussian curve and subtracted from the measured curve. Similar curves (0.48-mrad slits) were measured at − 110 and − 80 °C. An increase in temperature decreases the height of both the central peak and the side peaks. For example, in the [10$\bar{1}$0] curve the relative height of the peak a over the local minimum is about 2% at − 80 °C compared to about 6% at − 148 °C. A 20° rotation of the [10$\bar{1}$0] sample around the z direction did not change the curve. Also, two different [0001] samples gave identical curves. Some groups[1,2] claim to have seen effects due to such rotations for metal single crystals. We therefore wanted to test this also for single crystals in which positronium is formed.

We interpret our results as evidence of a delocalization of positronium (Ps) in ice in agreement with the recent interpretation[3] of angular-correlation measurements in quartz single crystals.[3,4] Both the central and the side peaks are ascribed to para-Ps annihilation, while the rest of the curve is due to pick-off annihilation of ortho-Ps and annihilation of positrons not forming Ps. In the nonrelativistic approximation the spin-averaged 2γ-annihilation probability of para-Ps is given by

$$dw \propto \left| \int e^{-\vec{k}\cdot\vec{x}}\, \psi(\vec{x},\vec{x})\, d\vec{x} \right|^2 d\vec{k}\, d\Omega \ . \tag{1}$$

$\psi(\vec{x}_e, \vec{x}_p)$ is the Ps wave function, $\vec{k}$ the sum of the photon wave vectors, and $d\Omega$ is the space-angle element for one of the photons ($\hbar = c = 1$).

A reasonable assumption is to put $\psi(\vec{x}_e, \vec{x}_p) = X(\vec{r}) f(\vec{R})$, i.e., a product of a function $X(\vec{r})$ of the center-of-mass coordinate $\vec{r} = \frac{1}{2}(\vec{x}_e + \vec{x}_p)$ and a function $f(\vec{R})$ of the relative coordinate $\vec{R} = \vec{x}_e - \vec{x}_p$, e.g., the s-state wave function. [This assumption is not necessary, i.e., we would also get an equation like (2), if we just assumed $\psi(\vec{x},\vec{x})$ in (1) to be a Bloch function.] We assume that Ps is delocalized in the center-of-mass motion, i.e., $X(\vec{r})$ is a Bloch function in agreement with the translational invariance of the lattice. We can then put

$$X(\vec{r}) \propto e^{i\vec{p}\cdot\vec{r}} \sum_{\vec{g}} a_{\vec{g}}\, e^{i\vec{g}\cdot\vec{r}} \ ,$$

where $\vec{p}$ is the crystal wave vector and $\vec{g}$ is a vector in the reciprocal lattice. Hence

$$dw \propto \sum_{\vec{g}} |a_{\vec{g}}|^2 \delta(\vec{p} - \vec{k} + \vec{g})\, d\vec{k}\, d\Omega \ .$$

The setup determines, in a good approximation,

$$dw_1 \propto \int_{\Delta\Omega} d\Omega \int_{-\infty}^{\infty} dk_x \int_{-\infty}^{\infty} dk_y \sum_{\vec{p}} S(\epsilon(\vec{p})) \times \sum_{\vec{g}} |a_{\vec{g}}(\vec{p})|^2 \delta(\vec{p} - \vec{k} + \vec{g})\, dk_z \tag{2}$$

folded with the angular-resolution curve. Here $S(\epsilon(\vec{p}))$ is the Maxwellian distribution, and $\Delta\Omega$ is the effective detector area. Peaks may therefore occur at angles $\theta = 2\pi\hbar g_z/mc$, where g_z is the projection of $\vec{g}$ on the z direction. The contribution of

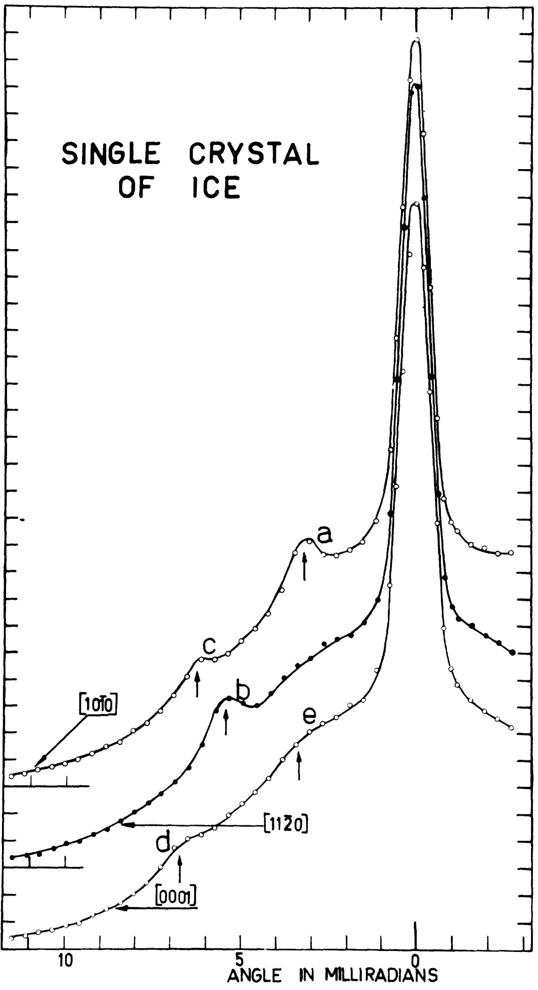

FIG. 1. Angular-correlation curves for ice single crystals. Arrows indicate the theoretically calculated centers of the side peaks. The curves are normalized to equal areas.

a reciprocal-lattice point $\vec{g}$ is given by

$$I_{\vec{g}} = \sum_{\vec{p}} S(\epsilon(\vec{p}))\,|a_{\vec{g}}(\vec{p})|^2 \,.$$

Only states $\vec{p}$ for $|\vec{p}| \ll |\vec{g}|$, $|\vec{g}| \neq 0$ are occupied, because para-Ps is thermalized or nearly thermalized. Hence the forms of the side peaks are nearly identical with the form of the central peak, only the intensities are lowered. This is clearly shown in Fig. 2 where the full widths at half-maximum (FWHM) are equal to 0.72 ± 0.03 mrad for all peaks. $|a_{\vec{g}}|^2$ is only different from zero for small $\vec{g}$. The peaks *a*, *b*, and *c* in Figs. 1 and 2 are therefore mainly due to the distributions $I_{\vec{g}} \simeq 0.045 I_{\vec{0}}$ for $\vec{g}$ equal to (±1, 0, 0), (0, ±1, 0), (1, −1, 0), and (−1, 1, 0) (structure factor $|S|^2 = 4$). Peaks *a* and *b* get contributions from two reciprocal-lattice points, while only one point contributes to *c*. This explains why peaks *a* and *b* have nearly equal intensities, and the intensity of peak *c* is half that of the other two peaks. An intensity of $0.025 I_{\vec{0}}$ for $\vec{g}$ equal to (0, 0, ±2) ($|S|^2 = 8$) may give the peak *d* in the [0001] curve. Points (0, 0, ±1) have $|S|^2 = 0$. Hence the small hump around *e* may be ascribed to the small intensities at all the points of types (1, 0, 1) ($|S|^2 = 1.75$).

The widths of the peaks in Fig. 2 cannot be completely explained by the normal causes of smearing. The FWHM due to the (a) Maxwellian distribution (normal mass, $T = 125\,^\circ$K) 0.25 mrad, (b) finite slit widths 0.24 mrad, and (c) uncertainties in the effective sample height 0.3 mrad, give altogether about 0.5 mrad, compared with a measured width of 0.72 mrad. The difference can be caused by not completely thermalized para-Ps or by the effective mass of para-Ps being smaller than the normal mass.

The relative intensity of para-Ps annihilation, i.e., the relative area of the central plus the side peaks, is (15.2 ± 0.4)% for all curves. The intensity I_2 of the longer lifetime $\tau_2 = 0.6$ nsec in pure poly-

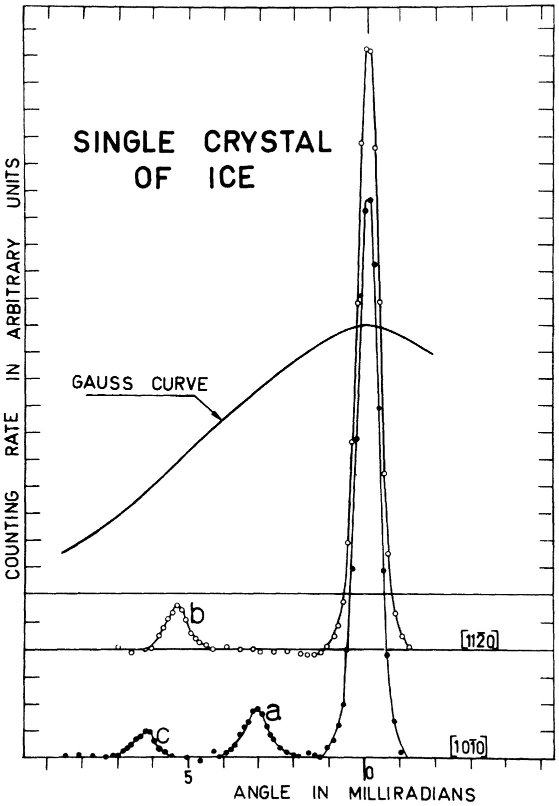

FIG. 2. Parts of the angular-correlation curves measured with high resolution. The broad component was fitted by the shown Gaussian curve and subtracted from the measured curve. The curves are normalized to equal areas.

crystalline ice is difficult to determine, because τ_2 is comparable to the shorter lifetime τ_0 due to "free" annihilation of positrons.[5] However, for concentrations above about 10^{-4} mole/liter of HF or HCl in polycrystalline ice at − 160 °C, τ_2 increases to 1.2 nsec.[5] This is interpreted as trapping of ortho-Ps in holes in the structure (perhaps L defects) created by the impurities. The corresponding intensity I_2 is easily found to be $(47 \pm 1)\%$, i.e., approximately equal to three times the para-Ps intensity found above. Assuming that such dilute concentrations will not change the Ps-formation probability this indicates (as also found at higher temperatures[6]) that no ortho-para conversion occurs in ice around − 150 °C.

Recently the interaction of ortho-Ps with free radicals in octanol and benzene was found to be much stronger in the solid than in the liquid phase.[7] An explanation of this might be that the movement of Ps in the condensed phase resembles that of an electron in a metal rather than a diffusion of the usual type with an exponentially decreasing diffusion constant for decreasing temperature. The higher degree of order in the solid phase would then imply a faster Ps transport and thus a stronger interaction. The fact that Ps is delocalized in ice and quartz supports this point of view. Our results also raise the problem of whether or not other atoms (e.g., myonium and hydrogen) are delocalized in ice. The answer to this problem would be of importance for the interpretation of, e.g., radiation-chemistry experiments in ice.

We will continue our measurements by investigating the side peaks as a function of temperature in H_2O and D_2O single crystals. In particular, the sudden change in the width of the narrow component around − 20 °C in H_2O and around − 30 °C in D_2O[8] found in polycrystalline ice will be examined. Also, a magnetic quenching experiment on ice single crystals is under preparation. A complete trapping of para-Ps must cause a disappearance of the side peaks in the angular-correlation curves. In order to investigate this problem we are presently preparing HF-doped single crystals of ice for further lifetime and angular-correlation measurements.

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