Evidence for nonexistence of self-trapped positronium in KI at very low temperatures

T. Hyodo, M. Kakimoto,* Y. Nagashima, and K. Fujiwara
Institute of Physics, College of Arts and Sciences, University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153, Japan
(Received 30 May 1989)

The polarization effect of a magnetic field on the positronium components in the one-dimensional angular correlation of annihilation radiation in KI has been investigated. It has been confirmed that practically all positronium atoms annihilate from the free states at 15 K. Rapid increase in the fraction of the positronium atoms annihilating from the self-trapped state with increasing temperature is also confirmed. An interpretation of the results is given in terms of the metastable self-trapping of positronium suggested previously. The self-trapping of positronium is discussed in connection with that of excitons.

Very sharp peaks due to the annihilation of free-positronium (Ps) atoms are observed at low temperatures in the angular correlation of annihilation radiation (ACAR) spectra for such alkali halides as NaF, NaCl, NaI, NaBr, KCl, KBr, KI, and RbCl.[1–6] There is a second group of alkali halides (LiF, KF, CsI) in which a free-Ps peak has been observed neither at room temperature nor around 10 K,[2,4] although the existence of a Ps or Ps-like system has been confirmed at least for LiF.[7] It has also been observed that the free Ps in the first category of alkali halides gets localized as the sample temperature is elevated. The localization has been attributed to the self-trapping of the Ps.[4,8–11] Similar coexistence of the free and self-trapped components has been observed in the exciton-luminescence spectra in alkali iodides[12] and other ionic crystals,[13,14] rare-gas solids,[15] and molecular crystals.[16,17] In these exciton cases, however, the intensity of the free component is much lower than the self-trapped component at any temperature. This leads to a question of whether the self-trapped Ps component in the first category of alkali halides is really negligibly small at low temperatures, as was tacitly assumed in the previous analysis.[4,10,11]

While the two components in the exciton luminescence are usually well separated from each other, those in the ACAR are both centered at zero momentum. This is because the former is the energy spectrum and the latter is the momentum spectrum. Moreover, in the ACAR the components other than that from the 2γ self-annihilation of Ps are also centered at zero momentum. Thus, one must be careful in analyzing and interpreting the ACAR data. In the previous analysis[4,10] the data at the lowest temperature were decomposed into a smooth "broad component" and narrow, free-Ps peaks (including side peaks arising from the Bloch nature of the Ps wave function[18]). It was further assumed that the shape of the "broad component" was independent of temperature, and at higher temperatures the Ps momentum distribution was determined by subtracting the same "broad component" from the data. It is highly desirable to examine the validity of this assumption with an independent method. The assumption has been partly supported by the observation that the ACAR for LiF, in which no Bloch Ps peak is observed, does not show such a drastic change with rising temperature as those for the first-category alkali halides.

In this paper we report high-resolution one-dimensional (1D) ACAR measurements in magnetic fields. The results show conclusively that practically all the Ps atoms annihilate from the free states in KI at 15 K. It is also shown that the previous analysis based on the assumption of the temperature-independent "broad component" is essentially valid.

A KI sample was cleaved from a slab of optical-grade single crystal supplied by Harshaw. It was shaped into a wedge of about $25\times16\times3.5$ mm^3 and etched with a mixture of water and methanol while keeping one of the surfaces as cleaved. The cleavage surface was used to set the sample so that the $\langle 100\rangle$ axis of the crystal was parallel to the measured momentum direction. The sample was mounted on a cold finger of a closed-cycle helium refrigerator fitted to a vacuum-tight chamber. The sample temperature was controlled within ±0.5 K when it was below room temperature; one measurement was done at about $T=305$ K without controlling. The sample was enclosed by a copper thermal-radiation shield with a 17-μm Al window for the incident positrons. The sample chamber also had a window of 40-μm Be. A ^{22}Na positron source was placed in the atmosphere just outside the Be window. The chamber was placed between the 32-mm-gap pole surfaces of an electromagnet. The optical resolution of the apparatus was $0.37\times10^{-3}mc$ (in momentum), where c is the speed of light in vacuum.

The 1D ACAR measurements were performed under magnetic fields of flux density $B=1.6$ T. At each point of the scan the coincidence counts were accumulated first with **B** pointing parallel to the average momentum of the positrons impinging on the sample, and then with **B** reversed. The magnetic field mixes the *para*-Ps state with the $m_s=0$ substate of *ortho*-Ps. The mixing increases the 2γ self-annihilation of the Ps, leading to an enhancement of the Ps component in the ACAR data. This effect is sometimes called magnetic quenching because it accompanies the shortening of the mean lifetime of the $m_s=0$ *ortho*-Ps. The effect is larger when **B** is parallel to the positron spin than when antiparallel.[18,19] The difference

 ©1989 The American Physical Society

can be observed by switching the polarity of **B** without changing its magnitude because the positrons from a β^+ decay source are spin polarized along their momentum. As pointed out by Lee *et al.*,[20] the quenching effect is less simple to interpret than the polarization effect because the positron beam diameter depends on $|\mathbf{B}|$. Though the problem of $|\mathbf{B}|$-dependent resolution[20] is not serious in 1D ACAR, the change in the effective diameter of the sample still leads to uncertainty in the interpretation of the data for materials liable to get radiation damage. We thus performed the polarization experiments, comparing the ACAR data for **B** parallel to the positron momentum direction, $I_{\mathbf{B}}(p_z)$, with those for **B** antiparallel, $I_{-\mathbf{B}}(p_z)$.

The polarization effect can be demonstrated by the direct difference of the ACAR data, $D(p_z)=I_{\mathbf{B}}(p_z)-I_{-\mathbf{B}}(p_z)$, which has been used to show the existence of Ps in quartz[18] and intercalated graphite.[20] However, the shape of $D(p_z)$ is not simple because it represents (Ps component) − (pickoff component). It is, at least approximately, possible to separate the Ps component from the polarization data by constructing a modified difference

$$D_\xi(p_z)=I_{\mathbf{B}}(p_z)-\xi I_{-\mathbf{B}}(p_z)\ . \tag{1}$$

To describe the idea let us denote the ACAR in the field **B** by

$$I_{\mathbf{B}}(p_z)=\alpha(\mathbf{B})P(p_z)+\beta(\mathbf{B})Q(p_z)\ , \tag{2}$$

where $P(p_z)$ is the Ps component, i.e., the component from the 2γ self-annihilation of Ps, and $Q(p_z)$ the remainder. Equation (2) includes an approximation that the shape of the ACAR from the annihilation of non-Ps positrons and that from the pickoff annihilation of Ps, which are both mainly determined by the momentum distribution of the valence electrons, are described by the same function, $Q(p_z)$. If one chooses the value of ξ equal to $\beta(\mathbf{B})/\beta(-\mathbf{B})$, then Eq. (1) becomes

$$D_\xi(p_z)=[\alpha(\mathbf{B})-\xi\alpha(-\mathbf{B})]P(p_z)\ , \tag{3}$$

which represents the momentum distribution of the Ps itself. The value for ξ must be carefully determined because $D_\xi(p_z)$ depends on it rather sensitively.[21] Fortunately, it is possible to deduce an appropriate value of ξ from the experimental data. Since, in general, the Ps momentum distribution $P(p_z)$ is considerably narrower than the momentum distribution of the valence electrons $Q(p_z)$, it is expected that the ratio

$$R(p_z)=I_{\mathbf{B}}(p_z)/I_{-\mathbf{B}}(p_z) \tag{4}$$

is equal to $\beta(\mathbf{B})/\beta(-\mathbf{B})$ for $|p_z|$ larger than some appropriate value p_c.

Figure 1 shows $R(p_z)$ for the data at 28 and 305 K. It can be seen that $R(p_z)$ is constant for $|p_z|>1\times10^{-3}mc$ at 28 K and for $|p_z|>4\times10^{-3}mc$ at 305 K within the experimental errors. Since the main purpose of the present work is to examine whether there exists appreciable intensity of Ps component other than the narrow free-Ps peak at low temperatures, we decided to use for all temperatures a common value $p_c=4.5\times10^{-3}mc$, which is considerably larger than the width of the free-Ps peak. The value of ξ for each temperature was determined by the weighted average of the $R(p_z)$ for the momentum regions $|p_z|>p_c$.

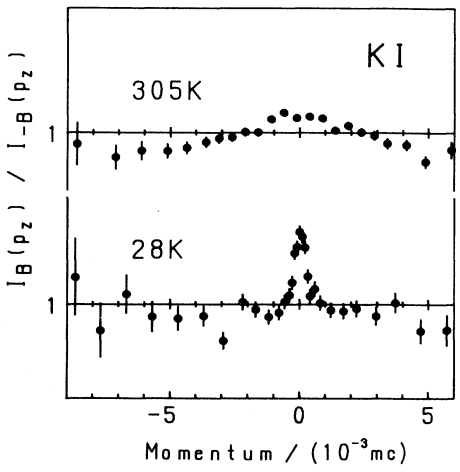

FIG. 1. Ratio between the ACAR data taken with magnetic fields of flux density 1.6 T parallel and antiparallel to the average positron momentum.

$D_\xi(p_z)$ thus obtained is plotted in Fig. 2. At 15 K only the very sharp free-Ps component is seen, showing that practically no Ps annihilates from a localized state, self-

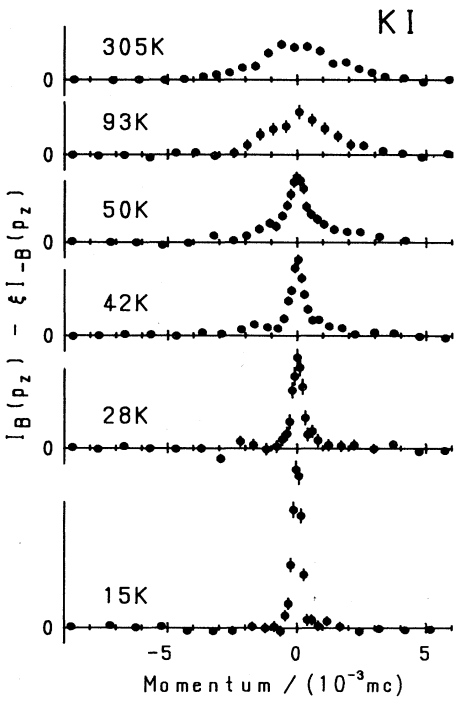

FIG. 2. Positronium momentum distribution in KI deduced by using the spin-polarization effect.

trapped or defect trapped. This clearly shows that Ps are first thermalized into the lowest free states and never localized during the course of the thermalization. A small tail, probably a Lorentzian tail due to phonon scattering,[22,23] is observed at 28 K. As the temperature is elevated to 42 and 50 K the component from the localized state appears. At 93 and 305 K most of the Ps atoms annihilate from the localized state.

All these features are consistent with the results of the analysis in the previous investigations.[4,10,11] (Note, in particular, the similarity between the data shown in Fig. 2 and those shown in Fig. 8 of Ref. 4.) This provides the first experimental evidence which supports convincingly the picture of the metastable self-trapped Ps state proposed in the previous works.

The self-trapped state of a simple particle or a composite particle like an exciton and a Ps atom results from the interaction of the particle with phonons.[24] The free and the self-trapped states are separated by an adiabatic potential barrier due to the short-range nature of the particle-phonon interaction. The barrier height and the energy level E_{ST} of the self-trapped state with respect to the lowest free state depend on the bandwidth of the particle, strength of the particle-phonon interaction, and phonon energy. When $E_{ST}<0$, or the self-trapped state is stable, the particle can tunnel through the barrier to relax into the self-trapped state even at lowest temperatures.[25,26] This is considered to be the case for the excitons in alkali halides. In KI at 4.2 K, for example, the free excitons can tunnel to the self-trapped state in about 160 ps,[27] 3 orders of magnitude shorter than the free-exciton-luminescence time, giving rise to much more intense self-trapped exciton luminescence than the free one.[12,28,29] If, on the other hand, $E_{ST}>0$ or the self-trapped state is metastable, then at very low temperatures, the particle cannot tunnel to the self-trapped state, because, in general, tunneling is possible only between states of the same energy. Thus, without phonons, i.e., at low temperature, the particle can decay only from the free state. It is highly probable that Ps in KI investigated in the present paper is this case. (Another possibility is that $E_{ST}<0$ but the trapping time is much longer than the Ps lifetime, ~ 100 ps,[30] at low temperatures. The time for the lattice relaxation necessary for the self-trapping is, in general, longer at lower temperatures.[26,31] Therefore, if, unlike excitons in KI, the Ps self-trapping time should be much longer than 100 ps even at 28 K, then this interpretation would be consistent with the present data.) As the temperature goes up, some of the Ps atoms get excited into free states at energy levels higher than E_{ST}, from which they can tunnel through the barrier. As the temperature gets even higher, thermal activation over the barrier to the self-trapped state also becomes possible. These cause a rapid increase in the self-trapped component as seen for Ps in KI.

It is to be noted that such a rapid increase is expected only in the case of the intrinsic self-trapping, where the possible localization sites are as many as the order of the number of the unit cells in the crystal. The importance of this "density of states" was first pointed out by Toyozawa and Sumi[32] and a discussion in connection with time-delayed trapping was in Refs. 4 and 11. Its good demonstration is perhaps found in the comparison between the temperature dependence of the exciton-luminescence spectra for the alkali iodides[27,28] and ZnSe-ZnTe alloys.[33] The former are examples of intrinsic self-trapping and the latter are those of impurity-induced self-trapping. In both cases, $E_{ST}<0$. In the intrinsic case where the number of the possible self-trapping sites is extremely large, an exciton once self-trapped stays so, since the thermal equilibrium distribution in the observed temperature range allows practically no free excitons. Thus the free-exciton luminescence is observed only not in thermal equilibrium at low temperatures. As the temperature is increased, the self-trapping rate increases and hence the already very low intensity of the free-exciton luminescence gets even lower. In the impurity-induced self-trapping case, on the other hand, thermal equilibrium may allow appreciable fractions of both free and self-trapped excitons and an increase in the free-exciton luminescence with increasing temperature is observed. A rapid increase in the trapping rate is also expected in the metastable self-trapping case ($E_{ST}>0$) when the trapping is intrinsic;[32] if the trapping of Ps in KI were defect or impurity induced, the increase in the annihilation from the self-trapped state would be much slower than that observed.[34]

In conclusion, we have measured the Ps momentum distribution by using the polarization effect of the magnetic field and obtained results which support the picture of the metastable self-trapped Ps.

Part of the present work has been presented at the International Conference on Positron Study of Fluids.[35] The present work was supported by the Japanese Ministry of Science, Culture and Education Grant No. 59460023. The experiments have been performed at the Radioisotope Center of the University of Tokyo.

---

*Present address: Information System Laboratory, Toshiba Research and Development Center, 1 Komukai Toshiba-cho, Saiwai-ku, Kawasaki-shi, Kanagawa 210, Japan.

[1]T. Hyodo and Y. Takakusa, J. Phys. Soc. Jpn. **42**, 1065 (1977).

[2]T. Hyodo and Y. Takakusa, J. Phys. Soc. Jpn. **45**, 795 (1978).

[3]J. Kasai and K. Fujiwara, J. Phys. Soc. Jpn. **51**, 3077 (1982).

[4]J. Kasai, T. Hyodo, and K. Fujiwara, J. Phys. Soc. Jpn. **57**, 329 (1988).

[5]K. P. Aref'ev, P. V. Kuznetsov, and O. V. Boev, Fiz. Tverd. Tela (Leningrad) **23**, 1877 (1981) [Sov. Phys.—Solid State **23**, 1098 (1981)]; K. P. Arefiev, O. V. Boev, P. V. Kuznetsov, and S. A. Vorobiev, Solid State Commun. **44**, 1067 (1982); K. P. Aref'ev, O. V. Boev, S. A. Vorob'ev, and P. V. Kuznetsov, Fiz. Tverd. Tela (Leningrad) **26**, 1678 (1984) [Sov. Phys.—Solid State **26**, 1017 (1984)].

[6]S. Linderoth, H. Rajainmäki, H. E. Hansen, and R. M. Niem-

inen, J. Phys. Soc. Jpn. **55**, 4504 (1986).
[7]A. Bisi, A. Dupasquier, and L. Zappa, J. Phys. C **4**, L311, (1971).
[8]Y. Takakusa and T. Hyodo, J. Phys. Soc. Jpn. **49**, 2243 (1980).
[9]T. Hyodo, J. Kasai, and Y. Takakusa, J. Phys. Soc. Jpn. **49**, 2248 (1980).
[10]J. Kasai, T. Hyodo, and K. Fujiwara, J. Phys. Soc. Jpn. **52**, 3671 (1983).
[11]T. Hyodo, in *Positron Annihilation,* edited by P. C. Jain, R. M. Singru, and K. P. Gopinathan (World Scientific, Singapore, 1985), p. 643.
[12]I. L. Kuusmann, P. Kh. Liblik, and Ch. B. Lushchik, Pis'ma Zh. Eksp. Teor. Fiz. **21**, 161 (1975) [JETP Lett. **21**, 72 (1975)]; I. L. Kuusmann, P. Kh. Liblik, G. G. Liid'ya, N. E. Lushchik, Ch. B. Lushchik, and T. A. Soovik, Fiz. Tverd. Tela (Leningrad) **17**, 3546 (1975) [Sov. Phys.—Solid State **17**, 2312 (1975)].
[13]I. L. Kuusmann, P. Kh. Liblik, and V. G. Plekhanov, Fiz. Tverd. Tela (Leningrad) **17**, 1854 (1975) [Sov. Phys.—Solid State **17**, 1218 (1975)].
[14]Z. A. Rachko and J. A. Valbis, Phys. Status Solidi B **93**, 161 (1979).
[15]J. M. Debever, A. Bonnot, A. M. Bonnot, F. Coletti, and J. Hanus, Solid State Commun. **14**, 989 (1974).
[16]A. Matsui and H. Nishimura, J. Phys. Soc. Jpn. **49**, 657 (1980).
[17]H. Nishimura, A. Matsui, and M. Iemura, J. Phys. Soc. Jpn. **51**, 1341 (1982).
[18]A. Greenberger, A. P. Mills, A. Thompson, and S. Berko, Phys. Lett. **32A**, 72 (1970).
[19]A. Bisi, A. Fiorentini, E. Gatti, and L. Zappa, Phys. Rev. **128**, 2195 (1962).
[20]R. R. Lee, E. C. von Stetten, M. Hasegawa, and S. Berko, Phys. Rev. Lett. **58**, 2363 (1987).
[21]A modified difference, $I_B(p_z)-\xi I_0(p_z)$, has been used in Von D. Herlach, Helv. Phys. Acta **45**, 894 (1972), and Ref. 5. In these investigations, however, the effect of the $|\mathbf{B}|$ dependence of the effective sample size was not checked and the values of ξ were determined rather arbitrarily.
[22]H. Ikari, J. Phys. Soc. Jpn. **46**, 97 (1979).
[23]K. Fujiwara, in *Positron Annihilation,* edited by P. G. Coleman, S. C. Sharma, and L. M. Diana (North-Holland, Amsterdam, 1982), p. 615.
[24]See, for example, Y. Toyozawa, J. Lumin. **24/25**, 23 (1981).
[25]K. Nasu and Y. Toyozawa, J. Phys. Soc. Jpn. **50**, 235 (1981).
[26]H. Sumi, J. Phys. Soc. Jpn. **53**, 3498 and 3512 (1984).
[27]Y. Masumoto, Y. Unuma, and S. Shionoya, J. Phys. Soc. Jpn. **51**, 3915 (1982); Y. Unuma, Y. Masumoto, S. Shionoya, and H. Nishimura, *ibid.* **52**, 4277 (1983).
[28]T. Hayashi, T. Ohata, and S. Koshino, J. Phys. Soc. Jpn. **42**, 1647 (1977); **43**, 347 (1977).
[29]H. Nishimura, C. Ohhigashi, Y. Tanaka, and M. Tomura, J. Phys. Soc. Jpn. **43**, 157 (1977); H. Nishimura and T. Yamano, *ibid.* **51**, 2947 (1982).
[30]T. Hyodo and A. T. Stewart, Phys. Rev. B **29**, 4164 (1984).
[31]D. Emin and A. M. Kriman, Phys. Rev. B **34**, 7278 (1986).
[32]Y. Toyozawa and A. Sumi, in *Proceedings of the 12th International Conference on the Physics of Semiconductors,* edited by M. H. Pilkuhn (Teubner, Stuttgart, 1974), p. 179.
[33]D. Lee, A. Mysyrowicz, A. V. Nurmikko, and B. J. Fitzpatrick, Phys. Rev. Lett. **58**, 1475 (1987).
[34]This trapping-site dependence of the trapping rate can be checked easily by using Eqs. (12) and (15) of Ref. 4.
[35]T. Hyodo, in *Positron Annihilation Studies of Fluids,* edited by S. C. Sharma (World Scientific, Singapore, 1988), p. 378.