PHYSICAL REVIEW B VOLUME 29, NUMBER 7 1 APRIL 1984

Anomalous temperature dependence of positron-lifetime spectra in KCl and NaF

T. Hyodo* and A. T. Stewart
Department of Physics, Queen's University, Kingston, Canada

(Received 7 February 1984)

Positron-lifetime spectra in KCl and NaF have been measured in the temperature range 9–353 K and 8–400 K, respectively. A large change in the spectra has been observed in the temperature range in which the angular-correlation data showed a transition from free to localized positronium. These experiments strongly support the hypothesis that at low-temperature Ps is in a free Bloch-like state while at high temperature it is localized, perhaps in a dilated interstitial region of the crystal.

Many crystals with sufficient space between the atoms show clear evidence that positronium can exist in an extended Bloch-like state. Other crystals show positronium atoms localized in some way. Some crystals, e.g., ice and alkali halides, show evidence of both free and localized positronium atoms.[1]

Recently Hyodo and Takakusa[2,3] discovered that in alkali halide crystals positronium existed in a free Bloch state at low temperatures. Further studies on NaF (Refs. 4 and 5) and KCl (Ref. 6) revealed that positronium became localized at high temperatures. This Rapid Communication reports lifetime experiments on the same alkali halides which show that the positronium atoms are in quite different states at high and low temperatues thus confirming the two-state picture, and the novel idea that as the temperature is increased, the Ps atoms change from the Bloch-like state to a localized state.

Specimens were optical-grade single crystal from Harshaw. The positron source was about 15 μCi of ^{22}NaCl sandwiched between a folded 1-mg cm^{-2} Ti foil. The radioactive area was about 15 mm^2. CsF scintillation crystals 2.5 cm diam × 2.5 cm long coupled to RCA 8850 photomultipliers were used as γ-ray detectors of a fast-fast time spectrometer. The high efficiency of the scintillator permitted us to collect half a million events in less than 2 h. The full width at half maximum of the time resolution was about 340 psec.

A helium flow cryostat of 2-cm o.d. was used for the temperature control. The measurements on each alkali halide were performed within four days. The whole temperature range was scanned every day; during the nights the sample was kept above room temperature while the data were accumulated. No appreciable time dependence, i.e., accumulated dose dependence of the spectrum was observed, although the samples were found very slightly tinged with color after the whole measurement.

The lifetime spectra were analyzed using a nonlinear least-squares program INTERACTIVE POSITRONFIT.[7] A two-component fit with only the background and the resolution function fixed was tried. The reduced χ^2 for the most of the set of data was close to unity. Analysis with more than two components was found to result in large uncertainties due to the correlation of the parameters. It was thus decided to examine the results of the two component analysis and interpret them allowing for the possibility of a number of contributions in each of the components. No correction for the source component was made although the spectrum for annealed Zn with the same positron source indicated a source component of 520 ps with intensity 2.7%

The results are shown in Figs. 1 and 2. In KCl, the intensity of the longer lifetime component, I_2, starts to increase at around 50 K and saturates at around 100 K, while in NaF it starts to increase at around 100 K and saturates at around 300 K. In the same temperature region the short lifetime, τ_1, decreases slightly in both the alkali halides. The long lifetime, τ_2, on the other hand, increases in KCl and decreases in NaF. It is quite interesting that the angular-correlation data have shown the transition from the free positronium to localized positronium in almost the same tempeature ranges.[4-6] This correspondence suggests that the phenomena are closely related.

To understand these data we postulate a model which includes free and trapped states for both positrons and for positronium. The model is simplified by assuming that at the lowest temperature the positronium atoms are all Bloch-like while at high temperature all positronium atoms are local-

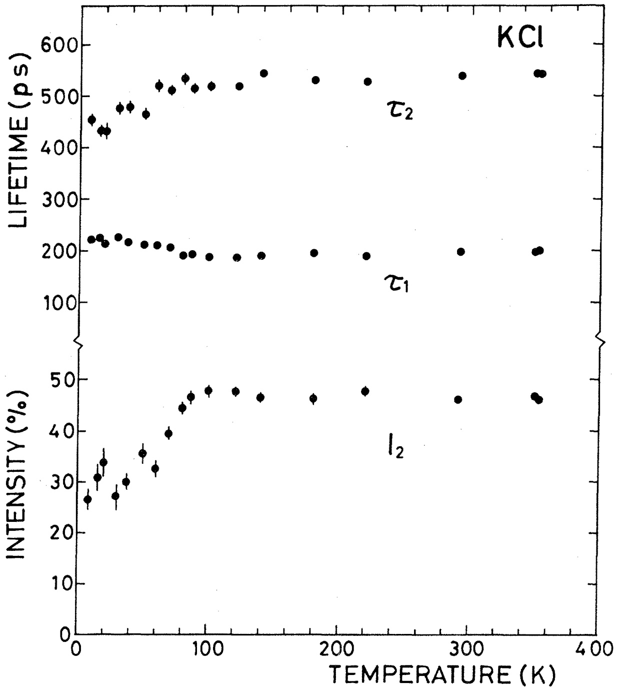

FIG. 1. The short lifetime (τ_1), the long lifetime (τ_2), and the intensity of the τ_2 component (I_2) in KCl. The statistical standard deviations are shown when they exceed the size of the points.

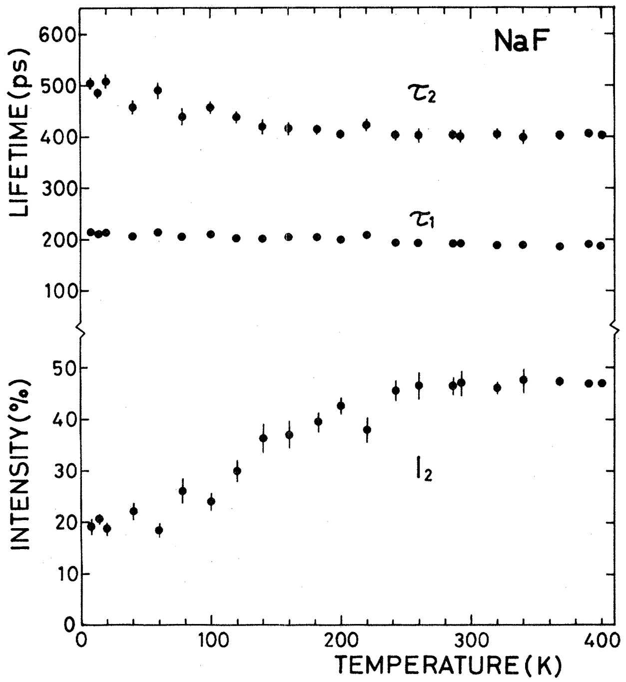

FIG. 2. The short lifetime (τ_1), the long lifetime (τ_2), and the intensity of the τ_2 component (I_2) in NaF. The statistical standard deviations are shown when they exceed the size of the points.

ized. (Some Ps atoms may also be trapped by vacancies. However, the fraction trapped should not change much over this temperature range and so need not be noted explicitly in the simple model discussed here.) All other trapping and annihilation rates are assumed temperature independent. Further we assume that the "pick-off" annihilation rate for the Bloch-state is very fast as for example for Ps in quartz.[8] In summary for the lifetimes, τ, and intensities, I, we postulate

$$I_1 = I_{f+} + I_{pPs} + I_{foPs} ,$$

$$I_2 = I_{t+} + I_{toPs} ,$$

$$\tau_1 = (I_{f+}\tau_{f+} + I_{pPs}\tau_{pPs} + I_{foPs}\tau_{foPs})/I_1 ,$$

$$\tau_2 = (I_{t+}\tau_{t+} + I_{toPs}\tau_{toPs})/I_2 ,$$

where the subscript t+ means trapped positron, f+ means free positron, fpPs means free parapositronium, etc. Note that we have assigned both free and trapped pPs to I_1, thus τ_{pPs} will appear temperature dependent.

Using the data of Table I, we can deduce the various lifetimes and intensities shown in Table II.

The fraction of the $\beta+$ which self-annihilates from a pPs state can be calculated to be 4% and 5% at low and high temperature in KCl. These figures compare well, within the 1–2% accuracy, with the observed narrow component in angular correlation data, viz., 3% and 6.5%, respectively.[6] For NaF the estimates from lifetime are 6% (Lo*T*) and 7% (Hi*T*) while the narrow component is about 2.5% and 3.5%.[9] These data are of course not precise enough to measure the distortion of the positronium atom in either state within the solid, although it seems that the atom is more "compressed" in the extended state than in the localized state.

The nature of the localization is not understood but some speculation about the site may be made. It is not likely a vacancy for several reasons: The lifetime of trapped Ps is usually longer,[10–13] the number of vacancies is usually not so much a function of temperature in this temperature range as of composition,[14] and the positron irradiation did not seem to influence the results.

A more likely site may be the tetrahedral interstice of the crystal. Kasai and Fujiwara suggested that the wave function of the Bloch positronium may have a large amplitude in this region.[15] Positronium could be self-trapped there if the volume were expanded by moving ions in the soft [110] directions. It may be worth pointing out that the tetrahedral interstice is fairly large even before any deformation; if the usually accepted ion radii[16] are assumed, the inscribed sphere to the interstice in most alkali halide crystals have a diameter larger than the Bohr radius of the free positronium in vacuum, 1.06 Å. The free volume in the interstice in the perfect cyrstal is larger in KCl than in NaF. Considering that the bulk modulus of KCl is less than half of that of NaF,[17] the difference may be increased after the deformation. This is consistent with the observation that the deduced pick-off lifetime of the localized positronium is much longer in KCl than in NaF. The self-trapped positronium atom suggested here is an identity resembling the self-trapped exciton, although the trapping site and the accompanying lattice deformation are different.

In summary, the long lifetime component in positron lifetime spectra in KCl and NaF is observed to increase remarkably in about the same temperature range for which the positronium peak in the momentum distribution shows anomalous broadening. The results are consistently interpreted if it is presumed that positronium, which is in the Bloch state at very low temperatures, is localized in a hole of its own digging at higher temperatures. The pick-off lifetime of the ortho positronium in the localized state has been deduced.

TABLE I. High- and low-temperature (Hi*T*, Lo*T*) characteristics of positrons annihilating in KCl and NaF (from Figs. 1 and 2).

	KCl		NaF	
	Lo*T*	Hi*T*	Lo*T*	Hi*T*
τ_1 (ps)	220 ± 5	200 ± 5	213 ± 3	190 ± 3
τ_2 (ps)	440 ± 10	540 ± 5	500 ± 5	405 ± 5
I_2	0.29 ± 0.3	0.47 ± 0.02	0.195 ± 0.02	0.47 ± 0.01

TABLE II. Deduced lifetimes and intensities of positrons and positronium in KCl and Naf.

		I	τ_f (ps)	τ_t (ps)
KCl	pPs	0.06 ±0.01	87 ± 7	106 ± 3
	oPs	0.18 ±0.04	286 ± 70	701 ± 150
	e_f^+	0.47 ±0.03	212 ± 17	· · ·
	e_t^+	0.29 ±0.03	· · ·	440 ± 10
NaF	pPs	0.09 ±0.01	83 ± 4	91 ± 5
	oPs	0.275 ± 0.02	260 ± 35	338 ± 60
	e_f^+	0.44 ±0.02	210 ± 20	· · ·
	e_t^+	0.195 ± 0.02	· · ·	500 ± 5

ACKNOWLEDGMENTS

The authors wish to thank Dr. R. J. Douglas, Dr. B. T. A. McKee, Dr. T. McMullen, and Dr. E. Zaremba for helpful discussions. One of the authors (T.H.) is indebted to Professor K. Fujiwara for drawing his attention to the importance of the tetrahedral interstice. He also acknowledges the travel support provided by Yoshida Foundation for Science and Technology. This work was supported by the National Science and Engineering Research Council of Canada.

---

[*] On leave from Institute of Physics, College of General Education, University of Tokyo, Tokyo, Japan.

[1] For recent reviews of this subject, see A. Dupasquier, in *Positrons in Solids,* edited by P. Hautojärvi (Springer, Berlin, 1979), p. 197; Also in *Positron Solid State Physics,* Proceedings of the International School of Physics "Enrico Fermi," edited by W. Brandt and A. Dupasquier (North-Holland, Amsterdam, 1983), p. 510; K. Fujiwara, in *Proceedings of the Sixth International Conference on Positron Annihilation, Forth Worth, Texas, 1982,* edited by P. G. Coleman, S. C. Sharma, and L. M. Diana (North-Holland, Amsterdam, 1982).

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

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

[4] Y. Takakusa and T. Hyodo, J. Phys. Soc. Jpn. 49, 2243 (1980).

[5] T. Hyodo, J. Kasai, and Y. Takakusa, J. Phys. Soc. Jpn. 49, 2248 (1980).

[6] J. Kasai, T. Hyodo, and K. Fujiwara, J. Phys. Soc. Jpn. 52, 3671 (1983).

[7] C. J. Virtue, R. J. Douglas, and B. T. A. McKee, Comput. Phys. Commun. 15, 97 (1978).

[8] C. H. Hodges, B. T. A. McKee, W. Triftshäuser, and A. T. Stewart, Can. J. Phys. 50, 130 (1972).

[9] Results of a reanalysis of the data published in Ref. 4 following the procedure in Ref. 6, i.e., with the shape of the nonpositronium component fixed.

[10] A. Dupasquier, Nuovo Cimento Lett. 4, 13 (1970).

[11] W. Brandt, A. Dupasquier, and G. Dürr, Phys. Rev. B 6, 3156 (1972).

[12] L. Smedskaer and S. Dannefaer, J. Phys. C 7, 2603 (1974).

[13] A. Bisi, L. Bosi, A. Dupasquier, and L. Zappa, Phys. Status Solidi B 69, 515 (1975).

[14] R. G. Fuller, in *Point Defects in Solids,* edited by J. H. Crawford, Jr. and L. M. Slifkin (Plenum, New York, 1972), Vol. 1, p. 103.

[15] J. Kasai and K. Fukiwara, J. Phys. Soc. Jpn. 51, 3077 (1982).

[16] L. Pauling, *The Nature of Chemical Bond,* 3rd ed. (Cornell University Press, Ithaca, 1960), p. 514.

[17] M. P. Tosi, in *Solid State Physics* edited by F. Seitz and D. Turnbull (Academic, New York, 1964), Vol. 16, p. 44.