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Positron motion and trapping in ionic crystals

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Measurements of the temperature effect on the time spectra of positrons annihilated in additively colored KCl show that the rate of positron trapping at F centers per unit F-center concentration is temperature independent in the range 7–300 °K. The discussion of this new result points out that the trapping process in ionic crystals is not diffusion limited, and, therefore, that the hypothesis, on which was based the derivation of published values of positron diffusion constants, is not confirmed. A secondary result of our experiment is that the mean life of the positron–F-center bound system decreases by ~ 5% when the temperature changes from 300 to 7 °K. This effect may be attributed to the volume decrease of the void where the system is localized.

I. INTRODUCTION

The use of positron-annihilation techniques for the study of crystal defects has stimulated interest in the related problems of positron motion and trapping. Various authors have investigated these problems in the case of metals: thorough discussions and references can be found in recent review papers by Brandt[1] and by Bergersen and Pajanne.[2] Much less is known about positron motion in ionic crystals; attempts to derive positron diffusion coefficients and mobility values from an analysis of trapping rates in defects have been made by Brandt *et al.*[3,4] and by the present authors.[5] In our opinion, however, the whole matter needs to be reconsidered to understand whether data concerning positron diffusion in ionic crystals can really be obtained from measurements of trapping rates; the conclusions of Refs. 1 and 2 have now made clear that this is not the case for metallic media. To provide an experimental basis for discussing this question, we have measured the temperature dependence of the capture rate of positrons by F centers. The knowledge of this dependence is the key to understanding the factors controlling the trapping process.

As a guideline for the present research, we have assumed that the positron fate in colored ionic crystals may be described by the trapping model that we briefly describe here. Slow positrons may be captured by F centers in competition with annihilation in defect-free zones of the crystal and with trapping at other lattice imperfections. The positron–F-center bound system thus formed, indicated as $A_+^\prime$ center, may subsist in four different spin states, like a positronium atom. The three orthostates display the same long mean life and contribute with one distinct component to the annihilation-time spectrum; the parastate is short-lived, and has not been resolved in the time spectrum, but originates a typical narrow component in the angular distribution of the annihilation photons. In the case of KCl, both these effects have been unambigously observed[6-9]; the mean life attributed to annihilation from orthostates is $\tau_3 \simeq 1$ nsec (subscript 3 refers to the three-component analysis of the time spectrum performed in Ref. 7). We have, therefore, used KCl as a convenient, well-characterized test material, but it is reasonable to assume that the main conclusions of the present work are valid for all ionic crystals.

II. EXPERIMENTAL METHOD

Our experiment consisted in measuring the time spectra of positrons annihilated in additively colored KCl at various temperatures from 300°K down to 7°K, and in observing the modifications occurring in the intensity I_3 and in the mean life τ_3 of the long-living component of the spectrum.

Crystals of KCl, cleaved from a stock purchased from K. Korth oHG, Kiel, were additively colored with F centers in the 10^{17}–10^{18} cm^{-3} density range following van Doorn's[10] method and quenched just prior to the experiment. A sandwich was formed with two KCl slices (1 mm thick) and the positron source (10 μCi of Na^{22} from a NaCl solution, deposited on a mica foil of 1 mg/cm^2 and covered with a similar one). This assembly was then enclosed in the tail section of a cold-finger cryostat, and exposed to the view of the gamma detectors of the timing system. During this manipulation and the subsequent annihilation experiment, the KCl samples were kept in darkness to avoid aggregate formation and to maintain the *F* center concentration at a stable level. A small cryostat was used for temperatures above 80°K and a larger one for runs descending to lower temperatures. The temperature was measured with a calibrated termocouple [Au (2.11-at.% Co)-Ag (0.37-at.% Au)] and stabilized within 2°K. The timing equipment was of standard type[13]; the full width at half-maximum (FWHM) of the prompt curve in the actual conditions of the experiment was either 320 or 440 psec depending on whether the small or the large cryostat was used, it being necessary, in the second case, to obtain, at the expense of the resolution, a larger intrinsic counting efficiency of the system to compensate for the increased distance between source and detectors and for the increased absorption in the walls of the low-temperature cell. The analysis of the data was performed with the POSITRONFIT computer program[14]; the spectra were decomposed into three components even when, with the 440-psec resolution, no substantial improvement of the goodness of fit was obtained in passing from a two- to a three-component fit. This fact has no influence on the results concerning the long-living component, whose variations are the object of the present work.

The stability of the *F*-center concentration is a crucial point in our experiment. Therefore it is important to note that *F*-centers introduced in KCl by additive coloration are thermally stable at room temperature[12] and that the irradiation effects are negligible in our case. This is demonstrated by the following double check: (i) the annihilation spectrum at room temperature remained reproducible after a whole series of measurements, typically lasting ten days; (ii) in a separate experiment, we have observed no significant changes of the optical absorption spectrum of KCl crystals with 5×10^{17} *F* centers/cm^3 maintained for two weeks in the same conditions of the actual time-spectrum measurement. The optical absorption measurements were performed by means of a Hitachi Perkin-Elmer spectrometer.

III. RESULTS

Our results for the mean life τ_3 and the intensity I_3 of the long-living component are collected in Table I, separately for the six samples examined; each value in the table is an average of several measurements.

TABLE I. Intensity and mean life of the long-living time-spectrum component in additively colored KCl, for six samples of different coloration density at temperatures from 7 to 300 °K.

Sample	Temperature (°K)	τ_3 (10^{-10}sec)	I_3 (%)
1	300	9.80 ± 0.07	28.5 ± 0.4
	145	9.50 ± 0.12	27.2 ± 0.8
	88	9.23 ± 0.09	28.6 ± 0.7
2	300	9.65 ± 0.03	26.2 ± 0.2
	193	9.55 ± 0.10	26.2 ± 0.6
	145	9.33 ± 0.07	26.5 ± 0.5
	88	9.34 ± 0.08	24.1 ± 0.5
3	300	9.65 ± 0.03	26.2 ± 0.2
	193	9.42 ± 0.11	26.5 ± 0.7
	145	9.49 ± 0.08	25.1 ± 0.5
	88	9.21 ± 0.11	25.2 ± 0.8
4	300	11.3 ± 0.08	17.0 ± 0.2
	78	10.2 ± 0.11	18.4 ± 0.5
5	300	10.2 ± 0.14	26.3 ± 0.7
	78	9.37 ± 0.22	30.4 ± 1.7
6	300	9.77 ± 0.07	17.9 ± 0.3
	78	9.66 ± 0.11	17.5 ± 0.5
	55	9.34 ± 0.12	18.5 ± 0.5
	7	9.22 ± 0.11	17.8 ± 0.4

For the mean lives of the two short-living components we find $\tau_1\simeq 1.5\times10^{-10}$ sec and $\tau_2\simeq 4.7\times10^{-10}$ sec at room temperature, with small variations (< 10%) for differently colored samples. These data are in good agreement with previously published results.[7] The corresponding inten-

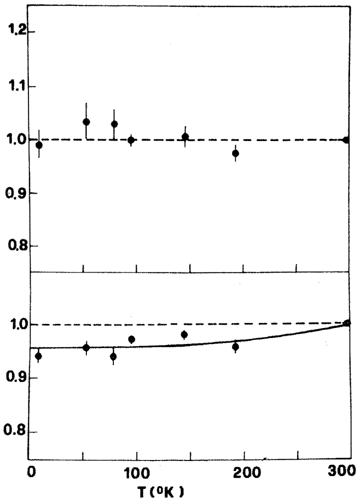

FIG. 1. Intensity and mean life of the long-living time-spectrum component in additively colored KCl, divided by the corresponding values at room temperature. The solid curve through experimental lifetime points represents the temperature dependence of the volume of a vacancy, normalized to 1 at room temperature.

sities I_1 and I_2 depend on the coloration density; for our samples, I_1 ranges from 13 to 27% and I_2 from 43 to 69%. The discussion of the physical significance of these two components is omitted here as it can be found in Refs. 7 and 11. Moreover, due to the insufficient resolution of the time spectrometer used for the low-temperature measurements, no discussion of the temperature dependence of the short-living components will be given here.

In Fig. 1 we report the ratios I_3/I_3^{RT} and $\tau_3/\tau_3^{\mathrm{RT}}$, where the superscript RT indicates the room temperature values. These ratios do not depend on the coloration density of the samples; an average of the results obtained with different samples was made. In the graph we also have shown (full line) the ratio V_v/V_v^{RT}, where V_v is the volume of an ion vacancy and V_v^{RT} is the corresponding value at room temperature. The curve has been calculated using the thermal expansion coefficients given by Meincke and Graham,[15] and assuming the validity of the relation

$$\frac{\Delta V_v}{V_v} = f\,\frac{\Delta V}{V}\ , \tag{1}$$

where $\Delta V/V$ indicates the relative thermal expansion of the bulk crystal, and f is a proportionality factor approximately equal to 2, as suggested by Jacobs.[16] As can be seen, the $\tau_3/\tau_3^{\mathrm{RT}}$ points fall close to this curve. A simple interpretation of this fact will be given in Sec. IV.

In the wide range of temperatures studied, no temperature effect has been noticed in the intensity I_3; according to the trapping model this means that the volume rate (trapping rate per unit trap density), ν, is also T independent. We may recall that, if escape from traps is neglected, I_3 and ν are related by the following equation:

$$I_3 = \frac{\nu N_F}{\tau_0^{-1} + \nu N_F}\ , \tag{2}$$

where N_F is the F-center density and τ_0^{-1} is the rate of all other processes competing with positron trapping in F centers. To fix the limits of a possible temperature dependence of ν, we tried to fit our data, assuming no temperature dependence for τ_0 and $\nu \propto T^x$, and we obtained $-0.02 \leqslant x \leqslant 0.02$. We should like to point out that the temperature independence of ν is probably the manifestation of a more general behavior than that simply indicated by the present research. For instance, also in the case of positron trapping by positive-ion vacancies no distinct temperature dependence has been observed in the 300–1000°K range.[4] There is also evidence for this same behavior for the capture in defects of metallic materials.[17]

IV. DISCUSSION

A few words may be said on the fact that the relative variations of the mean life τ_3 are of the same order as the relative volume variations of vacancies. This is precisely what is expected in agreement with the attribution of the related time spectrum component to the orthostate of an A_+' center. We may recall, in fact, that the A_+'-center orthostate decays essentially by pickoff annihilation with the electrons just around the center. The positron interaction with these electrons is partially screened by the A_+'-center electron, which, in turn, cannot give 2–γ annihilation because of angular-momentum conservation. A volume decrease of the void where the A_+' center is localized increases the positron probability of overlap with the electrons of the surrounding medium, and therefore decreases the lifetime by a corresponding amount.

In passing on now to the main result of our research, i.e., the observed T independence of the volume rate ν, and following the same line of analysis indicated by Brandt[1] in the case of trapping at metal defects, we shall discuss two opposite cases:

(i) The mean free path Λ for incoherent positron scattering is small compared to the mean distance d between traps. The trap is considered as a totally absorbing sphere of radius r_0. The capture rate thus coincides with the arrival rate at the defect.

(ii) Λ is long compared to d. The capture rate is determined by the transition rate from a delocalized positron Bloch state $|\vec{p}\rangle$ to a localized bound state $|l\rangle$.

Based on the assumptions of case (i), from the integration of the diffusion equation describing the positron motion in the bulk crystal, the following expression is obtained for the volume rate[18]:

$$\nu = 4\pi D_+ \Big/ \int_0^{1/r_0} \exp(eV/k_B T)\, d(1/r)\ , \tag{3}$$

where D_+ is the positron diffusion coefficient and V is the potential of the long-distance interaction between positron and F center. Substituting for V the expression

$$V = -\tfrac{1}{2}\gamma e/\epsilon^2 r^4\ , \tag{4}$$

where γ is the F-center polarizability and ϵ the static dielectric constant, and changing the upper limit of the integral in Eq. (1) from $1/r_0$ to ∞ [the condition $-eV(r_0) > k_B T$ is satisfied even at room temperatures for r_0 equal to the nearest-neighbor distance in KCl], Eq. (1) becomes

$$\nu = 4\pi D_+ \times 1.1 \left(\frac{\gamma e^2}{2\epsilon^2 k_B T}\right)^{1/4}\ . \tag{5}$$

Inserting in this formula the T-independent value of $\nu \simeq 10^{-8}$ cm^3/sec obtained from the results of Refs. 7 and 9, we have

$$D_+ \simeq 2\times 10^{-2}\left(\frac{T}{300\,^\circ\mathrm{K}}\right)^{1/4} \quad (\mathrm{cm}^2\,\mathrm{sec}^{-1})\,. \qquad (6)$$

To see if this result is reasonable, it is advisable to make a comparison with the information available concerning the electron diffusion constant D_- in ionic crystals. By means of the Nernst-Einstein equation $D = \mu k_B T/e$ we derive, from the Hall-mobility measurement of Brown and Inchauspé,[19] $D_- = 9\times 10^{-2}(T/300\,^\circ\mathrm{K}) \times \exp(300\,^\circ\mathrm{K}/T)$ cm^2 sec^{-1} in the temperature range where polar scattering with optical phonons dominates ($T > 50\,^\circ\mathrm{K}$), and $D_- \simeq 30(T/300\,^\circ\mathrm{K})$ cm^2 sec^{-1} in the lower temperature region, where acoustical phonon and impurity scattering becomes important. These values of D_- refer to a KCl crystal containing an F-center density of 3.4×10^{17} cm^{-3}, comparable to that of our samples. The D_+ expression in Eq. (3) differs from D_- by 1–3 orders of magnitude in the whole temperature range of our experiment. Actually, D_+ may differ substantially from D_- if positrons form bound systems with dislocations or even become trapped in shallow bound states around negative ions in defect-free zones of the crystal (trapping in positive-ion vacancies, or in vacancy clusters, is not important in additively colored crystals). We may attempt to account for this by defining an effective diffusion coefficient D_t proportional to the phonon-assisted hopping rate out of the trap, i.e.,

$$D_t = D_0 \exp(-E_b/k_B T)\,, \qquad (7)$$

and then writing

$$D_+^{-1} = D_-^{-1} + D_t^{-1}\,. \qquad (8)$$

However, no meaningful values of D_0 and E_b can be found that make Eq. (8) consistent with the experimental result expressed by Eq. (6). Therefore, we are led to conclude that diffusion is *not* the mechanism controlling positron trapping at defects in ionic crystals.

Turning now to the opposite capture-limiting situation (ii), i.e., $\Lambda > d$, we do not attempt to calculate the transition rate from the delocalized to the trapped state, but limit ourselves to noting that this rate is expected to be independent of T. The binding energy of a positron to an F center is not less than of 1.6 eV,[20] so that the energy to be transferred to the crystal will change by a negligible amount if the positron to be captured is not at the bottom of its energy band but has a kinetic energy of the order of $k_B T$. Moreover, the Bohr radius of the trapped state will, in any case, be small compared to the typical de Broglie wavelength of a thermal positron: this means that any matrix element connecting a delocalized Bloch state $|\vec{p}\rangle$ with the trapped state $|l\rangle$ will be practically independent of $\vec{p}$ in the absence of resonance. The above considerations are sufficient to make us conclude that the transition rate will be approximately the same for all incoming positrons of thermal energy, and then the resulting volume rate, averaged over the whole energy spectrum, will not depend on the temperature, in agreement with the experimental result. We recall that the same considerations apply to the case of positron trapping in metal vacancies.[2] The main difference between the case we are concerned with and that of metals is that the binding energy cannot be dissipated in an ionic crystal via electron-hole pair excitation, but only through radiation or multiphonon emission. This will not modify the T dependence, but will substantially decrease the probability of the transition process. In this respect, the volume rate calculated by Brandt[1] on the assumption of rapid energy dissipation, i.e.,

$$\nu = 4\pi r_0 \frac{\hbar}{\pi m_+}\,, \qquad (9)$$

has to be considered an upper limit for the actual rate in ionic crystals. In fact, Eq. (9), which works reasonably well for metals, gives a result two orders of magnitude larger than the experimental value for trapping by F centers in KCl.

V. CONCLUSIONS

The observed T independence of the positron capture rate in F centers shows that the trapping process is not diffusion limited. This suggests that we should be suspicious of positron diffusion coefficients and mobility values obtained through the analysis of positron trapping measurements. On the other hand, the present result also shows that one may confidently use positron techniques to obtain information concerning the nature and the concentration of defects without added difficulties resulting from a complicated temperature dependence of the volume rate. The experimental value of the volume rate in ionic crystals is definitely smaller than that calculated in the approximation of rapid energy dissipation. This fact accords with expectations, but an *ab initio* calculation, which is presently lacking, would be desirable.

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