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Three-Quantum Annihilation of Positrons in Ionic Crystals

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The three-quantum decay of positrons annihilating in lithium hydride, alkali halides, and alkaline-earth oxides was investigated using a triple-coincidence method. Relative measurements were made by comparing the three-quantum yield in each substance with that in aluminum, taken as a standard. In some cases the three-quantum yield was measured as a function of temperature and employing multicrystalline specimens or single crystals with and without color centers. The results suggest that the essential features of positron decay in alkali halides are connected with the properties of ideal crystals, while this is not true in alkaline earth oxides.

I. INTRODUCTION

Much quantitative and qualitative information on positron annihilation in ionic crystals is available at present. In fact, in addition to the angular-correlation data obtained on alkali halides some years ago,[1–3] new measurements have been performed on angular correlation in hydrides,[4] and lifetime spectra in hydrides,[5] alkali halides,[5,6] and alkaline-earth oxides.[7] The important feature of the lifetime spectra lies in their complexity: At least two components are shown. In alkali halides the decay rate characteristic of the second component exhibits an empirical regularity within each series and, at least in KCl, a static magnetic field is effective in quenching this component. These results have been interpreted as evidence for the formation of a positron bound system, in which the negative ion should play a predominant role.

The possibility of the occurrence of a positron bound system in ionic crystals has been investigated theoretically by various authors. In particular, the properties of the Ore complex H^-e^+ have been discussed with regard to its ground and excited states[8,9]; it appears that the experimental results could be interpreted on this basis. Gol'danskiĭ and Prokop'ev[10] have discussed two new kinds of bound states in alkali halides, besides the systems anion-e^+: (a) Pekar polaron state of the positron; (b) positrons captured by negative impurity or "host" ions in interstices of the lattice or by negative cation vacancies.

A quite different binding has been examined theoretically by Neamtan and Verral,[11] who found that the formation and persistence of positronium in ionic crystals is energetically allowed; such a system, however, deviates considerably from spherical symmetry.

No theoretical results are available to date on the three-quantum decay probability, which should be of importance for a more detailed knowledge of positron annihilation. Experimental data are scarce and obtained by means of indirect methods. Gainotti *et al.*[12] inferred the three-quantum yield in some alkali halides from the measurement of the small defect in the two-quantum annihilation rate in the energy spectrum. Bussolati and Zappa[7] measured the three-quantum yield in alkaline earth oxides by the "valley-to-peak" ratio method, which is conventional in the study of positron annihilation in gases. The two aforesaid experimental methods are intrinsically unable to give accurate results for solids, except in those cases where the three-quantum production is unusually large.

In this paper we report the results of a set of measurements performed by a triple coincidence method on the three-quantum annihilation yield for alkali halides, lithium hydride, and oxides of the second-group elements with a partial ionic binding. All the measurements were made at room temperature, but in some compounds we have also investigated whether the temperature affects the three-quantum production.

II. EXPERIMENTAL METHOD

The experimental setup used in the present investigation has been previously described.[13,14] We shall mention here only some essential points. The three-quantum yield was obtained by means of relative measurements, i.e., by comparing the triple-coincidence rate of positrons annihilating in the specimen under investigation with that in aluminum taken as a

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[1] G. Lang and S. De Bendetti, Phys. Rev. **108**, 257 (1957).

[2] W. E. Millet and R. Castillo-Bahena, Phys. Rev. **108**, 257 (1957).

[3] A. T. Stewart and N. K. Pope, Phys. Rev. **120**, 2033 (1960).

[4] A. T. Stewart and R. March, Phys. Rev. **122**, 75 (1961).

[5] A. Bisi, A. Fiorentini, and L. Zappa, Phys. Rev. **131**, 1023 (1963).

[6] A. Bisi, A. Fiorentini, and L. Zappa, Phys. Rev. **134**, A328 (1964).

[7] C. Bussolati and L. Zappa, Phys. Rev. **136**, A657 (1964).

[8] S. M. Neamtan, G. Darewych, and G. Oczkowski, Phys. Rev. **126**, 193 (1962).

[9] V. I. Gol'danskiĭ, A. V. Ivanova, and E. P. Prokop'ev, Zh. Eksperim. i Teor. Fiz. **47**, 659 (1964) [English transl.: Soviet Phys.—JETP **20**, 440 (1965)].

[10] V. I. Gol'danskiĭ and E. P. Prokop'ev, Fiz. Tverd. Tela **6**, 3301 (1964) [English transl.: Soviet Phys.—Solid State **6**, 2641 (1965)].

[11] S. M. Neamtan and R. I. Verral, Phys. Rev. **134**, A1254 (1964).

[12] A. Gainotti, E. Germagnoli, G. Schianchi, and L. Zecchina, Phys. Letters **13**, 9 (1964).

[13] M. Bertolaccini, C. Bussolati and L. Zappa, Phys. Rev. **139**, A696 (1965).

[14] M. Bertolaccini, C. Bussolati and S. Cova, Nucl. Instr. Methods (to be published).

TABLE I. Experimental results on the positron annihilation in ionic crystals: P/P_0 is the ratio between the three-quantum annihilation probability in the specimen in question and the same probability in Al. I_2 and τ_2 are the intensity and lifetime of the second component in the time spectrum. Δ is the difference, according to Eq. (1), between the measured relative three-quantum yield and the one calculated on the assumption that the I_2 component is due to positronium decay.

Crystal	P/P_0	I_2[a] (%)	τ_2[a] (10^{-10} sec)	Δ	Notes
LiH	0.94±0.05	absent			Single crystal
LiF	1.64±0.05	70 ±15	4.02±0.20	+(0.76±0.08)	Multicrystalline
NaF	2.32±0.04	49 ± 5	5.05±0.35	+(1.22±0.07)	Multicrystalline
KF	1.41±0.04	33 ± 7	6.20±0.40	+(0.24±0.07)	Multicrystalline
CsF	1.32±0.04	46 ± 5	7.60±0.21	−(0.01±0.08)	Multicrystalline
LiCl	1.38±0.04	30 ±10	4.25±0.25	+(0.44±0.05)	Multicrystalline
NaCl	1.27±0.04	52 ±15	4.96±0.24	+(0.22±0.06)	Multicrystalline
	1.28±0.04	60 ±15	5.11±0.25		Single crystal without color centers
	1.25±0.04				Single crystal with color centers (5×10^{16} cm^{-3})
KCl	1.32±0.03	50 ±15	6.07±0.12	+(0.17±0.07)	Multicrystalline
RbCl	1.30±0.04	31 ±10	6.27±0.19	+(0.19±0.06)	Multicrystalline
CsCl	1.31±0.04	25 ± 4	6.39±0.18	+(0.21±0.05)	Multicrystalline
LiBr	1.31±0.04	85 ±10	4.58±0.20	+(0.21±0.08)	Multicrystalline
NaBr	1.29±0.04	34 ± 7	5.56±0.20	+(0.19±0.05)	Multicrystalline
KBr	1.42±0.05	37 ± 7	6.73±0.22	+(0.15±0.07)	Multicrystalline
CsBr	1.34±0.05	31 ± 4	6.84±0.33	+(0.18±0.06)	Multicrystalline
NaI	1.40±0.04	61 ± 9	5.11±0.18	+(0.27±0.07)	Multicrystalline
KI	1.23±0.04	43 ± 7	6.40±0.21	+(0.07±0.06)	Multicrystalline
RbI	1.22±0.04	56 ±15	6.36±0.18	−(0.04±0.09)	Multicrystalline
CsI	1.15±0.03	25 ± 4	6.36±0.29	−(0.02±0.05)	Multicrystalline
BeO	22.5 ±0.4	6.8 ± 0.2	34.6 ±2.6		Multicrystalline
MgO	8.61±0.17	1.8 ± 0.1	48.6 ±5.2		Multicrystalline
	1.14±0.04	absent			Single crystal
CaO	2.75±0.07	3.2 ± 0.3	37.5 ±2.8		Multicrystalline
BaO	1.41±0.04	0.64± 0.07	32.0 ±2.7		Multicrystalline

[a] See Refs. 6 and 7.

standard. The source of positrons (about 40 μCi of Na^{22} from a carrier-free solution) was sealed into thin polypropylene foils (1.2 mg/cm^2) and put in a composite sandwich of four targets, two of which are the specimen under investigation, and the other two, the Al standard. The measurements consisted of several counting runs taken alternately with the sandwich arranged with the specimen inside and the Al outside, and conversely. The specimens were multicrystalline analytical reagent-grade chemicals (supplied by the B.D.H. Laboratory Chemicals Division, Poole, England); in a few cases (see Table I), single crystals were used too. All the results were corrected in order to account for a small fraction of annihilation events occurring in the polypropylene foils, following the procedure previously adopted.[13] The correction amounts to only a few percent.

The temperature effect on the three-quantum yield was investigated by using an active source on thin mica foil and multicrystalline specimens enclosed in a hermetically sealed container.

III. RESULTS AND DISCUSSION

Table I collects the experimental values of the ratio of the three-quantum annihilation probability P in the specimen in question to the same probability P_0 in Al. It appears that, in general, this probability exceeds that typical of metals, for which it is customary to take the value predicted by Ore and Powell[15] ($P_0 = 2.70 \times 10^{-3}$) on the assumption of annihilation with free electrons. A recent experimental result, in strict agreement with the Ore-Powell evaluations, is due to Bertolaccini *et al.*[13] who, found, for Al, $P_0 = (2.65 \pm 0.08) \times 10^{-3}$, employing the same experimental apparatus used in the present investigation.

In what follows, we shall examine all our results in the framework of present knowledge. For convenience, the various groups of compounds have been examined separately from the thermal effects.

A. Lithium Hydride

The time-annihilation spectrum of positrons in LiH, first investigated by Bisi *et al.*,[5] appeared to be complex: Besides a short-lifetime component I_1 of 2.1×10^{-10} sec, there was a long-lifetime component I_2 of 1.5×10^{-9} sec with an intensity of about 6%. According to Gol'danskiĭ *et al.*[9] the I_1 component could correspond to the annihilation from the first two excited levels of the system H^-e^+, while the I_2 component should come from the series of higher levels. Moreover, these authors found that the time spectrum should contain a third component of about 10^{-11} sec, corresponding to annihilation from the ground state, which has not been detected until now.

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[15] A. Ore and J. L. Powell, Phys. Rev. 75, 1696 (1949).

By employing different specimens of LiH, we have ascertained, through time-spectrum analysis, that the I_1 component is always characterized by the same mean life, while the I_2 component exhibits different intensities and mean lives depending upon the particular specimen employed. This fact is confirmed by a recent experimental result of Paulin and Ambrosino[16] who found a long lifetime of 2.1×10^{-9} sec with an intensity of 1.25%.

The relative three-quantum yield given in Table I refers to a specimen in which the I_2 component was practically absent. Within the experimental errors, P/P_0 is equal to 1, indicating that the spin state of the annihilating pair is singlet only one quarter of the time. This conclusion does not conflict with the known properties of the $H^- e^+$ system.

B. Alkali Halides

As can be seen from Table I, in most alkali halides the three-quantum decay probability exceeds the value characteristic of aluminum by about 30%. This corresponds to a three-quantum production larger than that expected by assuming that the I_2 component measured by Bisi *et al.*[6] is due to positronium decay.

Any attempt to find a clear and convincing correlation between these results and those extracted from the time spectra has been unsuccessful. One reason for this failure certainly lies in the fact that the intensities of the I_2 components have errors too large to allow a significant analysis of this type. A different attempt to correlate the experimental data is shown in Fig. 1 where we have plotted, as a function of the molecular density, the difference Δ between the measured relative three-quantum yield and the one calculated on the assumption that the I_2 component is due to positronium decay. The value of Δ was calculated according to the formula

$$\Delta = P_3/P_0 - (1-\tfrac{4}{3}I_2) + (1/P_0)I_2(\tau_2/\tau_3)\,, \qquad (1)$$

where τ_3 is the mean life of orthopositronium in free space. There is a tendency for crystals with higher molecular density to display a greater three-quantum excess. Two points must be taken in mind when considering this graph: (a) The Δ value for NaF was not reported, being exceptionally large; (b) In some time spectra by Bisi *et al.* there was a third component whose intensity is so faint that its contribution to three-quantum production, estimated according to the positronium assumption, is negligible.

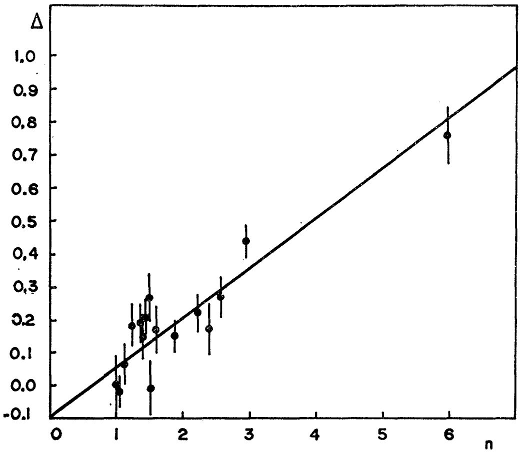

FIG. 1. Difference Δ, between measured and calculated three-quantum yields as a function of the molecular density n (units: 10^{22} cm^{-3}); calculated values are based on the assumption that the I_2 component is due to positronium decay.

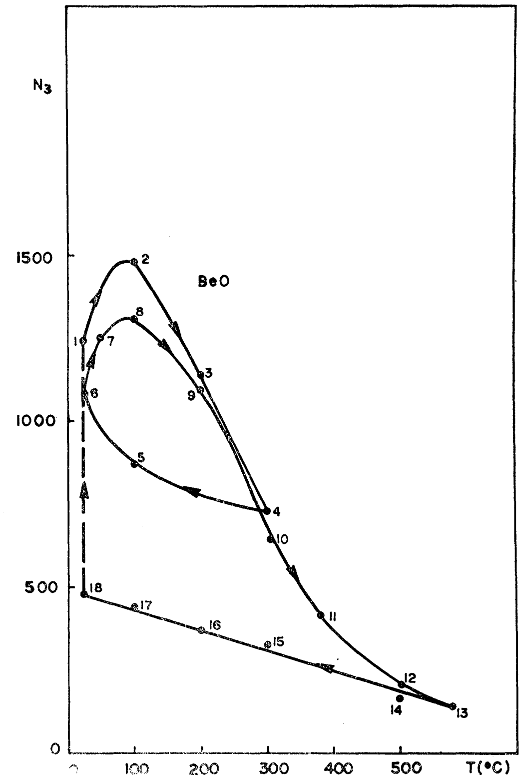

FIG. 2. Triple-coincidence rate (arbitrary units) in BeO, versus temperature. The numbers on the points indicate the measurement sequence.

Moreover, Table I shows that different samples of NaCl, multicrystalline and single-crystal with and without color centers, all display the same three-quantum yield. It appears, then, that the features of positron decay are insensitive to structural imperfections so that one can exclude those annihilation models based on deviations from a perfect homogeneous crystal lattice.

C. Alkaline-Earth Oxides

The three-quantum yield previously obtained by Bussolati and Zappa[7] with the "valley-to-peak" ratio

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[16] R. Paulin and G. Ambrosino, Compt. Rend. (to be published).

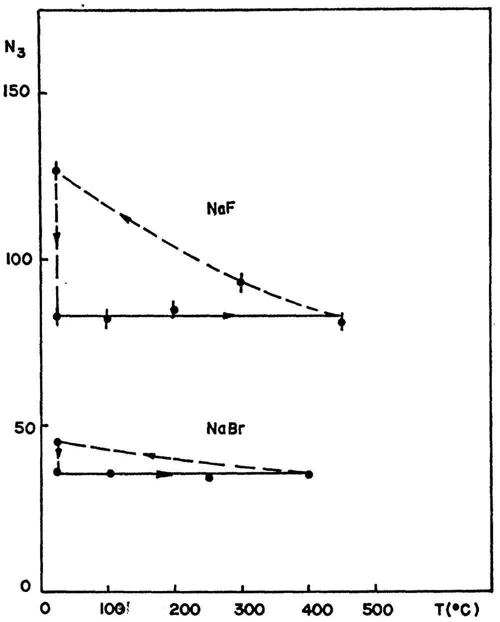

FIG. 3. Triple-coincidence rate (arbitrary units) versus temperature in NaF and NaBr.

method has been confirmed by the triple-coincidence measurements performed in the present investigation. As far as the behavior of positrons in these compounds is concerned, no theoretical information is at present available. Nevertheless it is reasonable to expect that the behavior can be different from that in alkali halides, because the crystal bond is not entirely ionic and the chemical-physical properties are quite different. This conjecture is supported by the following experimental results. The relative three-quantum yield is unusually large and attains the values 22.5 and 8.6 for multicrystalline specimens of BeO and MgO, respectively. When, instead, single crystals of MgO are used to absorb the positrons the P/P_0 value drops to unity. Moreover, in BeO the temperature affects the three-quantum yield in a striking way and to an extent which depends on the history of the specimen. Further evidence of the influence of the history and nature of the specimen on the annihilation features can be obtained by observing the lifetime spectra. In Table I we have reported the I_2 and τ_2 values measured by Bussolati and Zappa[7]; in it can be seen the absence of long-life component in a single crystal of MgO. In addition, Paulin and Ambrosino[16] found, recently, values of intensity and lifetime quite different from those of Bussolati and Zappa.

D. Thermal Effects

The temperature effect on the three-quantum yield was investigated in BeO, NaF, NaCl, and NaBr in the temperature range 25 to 450°C. The obtained results are reported in Figs. 2 and 3 where the three-quantum yield, in arbitrary units, is plotted versus temperature, and the numbers on the points indicate the sequence of the measurements. The counting times for each temperature value were 1 and 10 h for BeO and alkali halides, respectively, while the temperature change required only a few minutes.

One immediately notices the existence in BeO of hysteresis phenomena, which are very hard to interpret; perhaps the ability of this substance to adsorb a large amount of gas might be important. It is worthwhile to note that the three-quantum yield has recovered its original value about one day after the whole thermal treatment (dashed line in Fig. 2).

In NaF and NaBr, the three-quantum yield does not change when the temperature is increased; when the specimen is cooled to room temperature an increase of three-quantum yield is observed, followed by a slow recovery to the original value. No effect at all is seen in NaCl. In conclusion it is reasonable to think that a quenching procedure can, in some cases, introduce partial and transient modifications of the positron decay, whose essential aspect anyhow depends on the properties of ideal crystals. However, in the case of alkaline-earth oxides no similar conclusion could be valid at all.

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