

Semi-Conductor-to-Metal Transition and Positron Annihilation in V_2O_3 (*).

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Summary. — Positron lifetime spectra in V_2O_3 have been recorded in the temperature range $(80 \div 300)^\circ\text{K}$ in which the transition to the metal state occurs. The occurrence of a complex positron time annihilation spectrum is ascribed to annihilations taking place in different positron band states. The positron lifetimes $\tau_1 = 1.94 \cdot 10^{-10}$ s and $\tau_2 = 4.74 \cdot 10^{-10}$ s are found to be constant in the explored temperature range. This is explained in terms of localization of positron and electron wave functions. The observed behaviour with temperature of the intensities of the decay components is discussed as being due to the screening effect of the conduction electrons on the repulsive action of the V^{3+} lattice ions.

1. — Introduction.

It is now well ascertained that positron time-annihilation spectra in ideal pure metals are generally fitted by a single exponential decay ⁽¹⁾. The same is true for semi-conducting elements and for semi-metals As, Sb and Bi, where a low-intensity tail in the lifetime spectra may be entirely due to spurious effects ⁽²⁾. In both these cases the annihilation rates are given by the average electron density at the site of the positron in the ground state of the one-positron-many-electron system, and full many-body calculations for a free

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⁽¹⁾ H. WEISBERG and S. BERKO: *Phys. Rev.*, **154**, 249 (1967).

⁽²⁾ R. FIESCHI, A. GAINOTTI, C. GHEZZI and M. MANFREDI: *Phys. Rev.*, **175**, 383 (1968).

electron gas are in reasonably good agreement with experimental results in alkali metals (3,4).

On the contrary, the most striking feature of positron annihilation in diatomic and polyatomic crystals is certainly the complexity of the lifetime spectra, that is the occurrence of competitive processes contributing, with comparable probability, to annihilation. In molecular substances this is normally explained by supposing that annihilation takes place from ortho- and para-positronium states (5). The same hypothesis cannot be advanced for ionic crystals, where the interstitial space available for the positronium atom is extremely limited with a consequent drop of the positronium internal binding energy (6). The model proposed by GOL'DANSKII *et al.* (7,8) in which different decay components are ascribed to annihilation in different positron bound states with the negative ion, can be sufficiently correct if suitably generalized. The complexity of lifetime spectra may in fact be understood regardless of the nature of the different positron states and not necessarily only when they are bound states with a single ion. The conditions are that the positron may be found with comparable probabilities in different states and that the various charge distributions for these positron states differ strongly from one other, in order to ensure that the corresponding lifetimes are easily resolved. The states available for a positron inside a crystal are solutions of a Schrödinger equation where the potential experienced by the positron has the periodicity of the crystal and in principle may be set up by knowing electron wave functions and crystal structure. This description may serve as a working hypothesis for a tentative interpretation of the observed decay features of the positron in media where the electron-positron correlations are described with sufficient accuracy by a suitable enhancement factor, following BRANDT *et al.* (9).

In this scheme, it would be very interesting to carry out positron lifetime measurements in substances where the potential experienced by the positron can be varied by large amounts. These experimental conditions are not easy to achieve, since one is limited to very special cases, such as the lower oxides of vanadium. In VO, V₂O₃ and VO₂ the strong ionic character of the chemical bonds gives rise to a strong potential experienced by the positron. This potential, however, may be gradually screened out by the presence of conduction electrons, whose concentration may be greatly varied by changing the temperature of

(3) S. KAHANA: *Phys. Rev.*, **129**, 1622 (1963).

(4) J. P. CARBOTTE and S. KAHANA: *Phys. Rev.*, **139**, A 213 (1965).

(5) W. BRANDT and J. SPIRN: *Phys. Rev.*, **142**, 231 (1966).

(6) A. FERRELL: *Rev. Mod. Phys.*, **28**, 308 (1956).

(7) W. J. GOL'DANSKII, A. V. IVANOVNA and E. P. PROKOP'EV: *Sov. Phys. JETP*, **20**, 440 (1965).

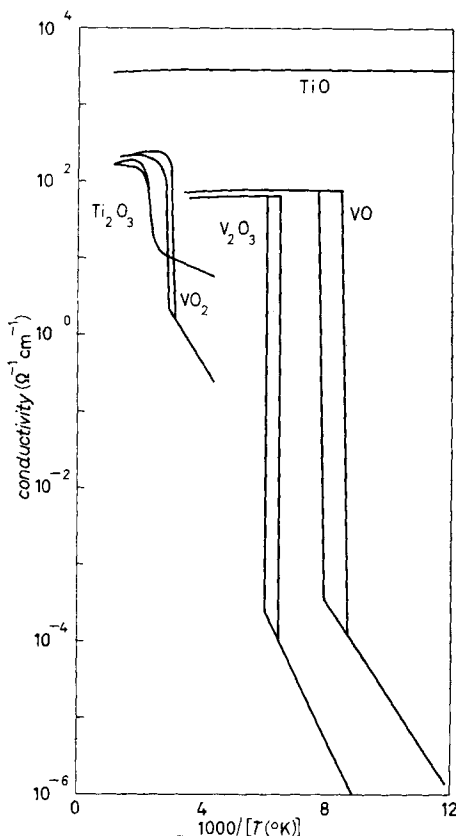
(8) A. V. IVANOVNA and E. P. PROKOP'EV: *Sov. Phys. JETP*, **21**, 771 (1965).

(9) W. BRANDT, L. EDER and S. LUNDQUIST: *Phys. Rev.*, **142**, 165 (1966).

the sample. These substances are in fact semi-conductors below a critical temperature, at which they show a sharp transition to the metal state. This behaviour was evidenced by means of electrical conductivity measurements and typical temperature-dependences of the electrical conductivity are given in Fig. 1, which shows the results of the experiments of MORIN⁽¹⁰⁾.

In this paper we report the results of time-spectra analysis of positrons annihilating in V_2O_3 in the temperature range $(85 \div 300)^\circ\text{K}$ including the characteristic transition temperature to the metal state. The experimental results are then discussed on the basis of the working hypothesis outlined in this Section.

Fig. 1. - Temperature-dependences of the electrical conductivity of the lower oxides of vanadium and titanium (F. J. MORIN: *Phys. Rev. Lett.*, **3**, 34 (1959)).



2. - Experimental method.

The experimental technique for the recording and analysis of the lifetime spectra has been described previously^(2,11). With narrow energy-selection windows set near the Compton edges of the ^{22}Na spectrum, the full width at half-maximum (FWHM) of the prompt-time resolution curve taken with the γ -rays emitted by ^{60}Co was $3.5 \cdot 10^{-10}$ s. The peak-to-background ratio was $10^4:1$ for the activities of the sources used in our experiments.

The positron lifetime measurements were made on V_2O_3 powder samples. In order to verify that our samples really undergo a semi-conductor-to-metal transition, we made some electrical conductivity measurements in the temperature range extending from 80°K to room temperature. In the low-temperature

⁽¹⁰⁾ F. J. MORIN: *Phys. Rev. Lett.*, **3**, 34 (1959).

⁽¹¹⁾ A. GAINOTTI, C. GHEZZI, M. MANFREDI and L. ZECCHINA: *Nuovo Cimento*, **56 B**, 47 (1968).

region, typically semi-conducting behaviour was evidenced: the resistivity increased exponentially with $1/T$, the activation energy being about 0.13 eV. This result is in substantial agreement with those of previous workers⁽¹²⁾. When the temperature was raised, a sharp transition to the metal state was observed at a critical temperature T_c ranging from 165 °K to 173 °K. The temperature of the transition from semi-conductor to metal in V_2O_3 has been variously reported as ranging from 168 °K in sintered materials to about 152 °K in single crystals. As was pointed out by FEINLEIB and PAUL⁽¹³⁾, the low transition temperature in single-crystal samples may be closer to the true transition point of pure material than the higher temperatures. Most impurities in V_2O_3 seem, in fact, to raise the transition temperature as well as to decrease the amount of resistivity change at the transition.

We may thus conclude that our samples certainly did contain some impurities (their nominal purity was in fact 99,9%) and perhaps some deviation from stoichiometry, but the most striking features in the temperature dependence of the electrical conductivity are not inhibited.

3. - Results.

A complex annihilation spectrum was observed for all the temperature values we examined: two decay components τ_1 and τ_2 , with comparable intensities I_1 and I_2 , were separated. In Fig. 2 typical spectra taken at the end points of the explored temperature range are shown. Data was analysed only from channels above a cut-off delay value, below which the decay curves deviate from double-exponential behaviour because of the finite instrumental time-resolution of the system. Each solid line is that best fitting the experimental data. As indicated in the Figure, the lifetimes τ_1 and τ_2 are nearly the same at 85 °K and 300 °K, whereas at 300 °K the fraction of the positrons annihilating by the slower process is considerably increased.

This behaviour is general, and in Fig. 3 the lifetimes τ_1 and τ_2 are shown to be quite constant over the explored temperature range. The arithmetic mean values taken over all measurements are $\tau_1 = (1.94 \pm 0.13) \cdot 10^{-10}$ s and $\tau_2 = (4.74 \pm 0.13) \cdot 10^{-10}$ s. In Fig. 4, the intensity I_2 of the slower component is plotted against temperature. For T lower than the transition temperature T_c , I_2 is found to increase continuously with temperature; I_2 then increases abruptly at the transition point and stays constant through the metal phase. It should be noted here that the annihilation spectra are taken one after another on heating the sample so that, even if present, a hysteresis cycle such as that

(12) D. ADLER, J. FEINLEIB, H. BROOKS and W. PAUL: *Phys. Rev.*, **155**, 851 (1967).

(13) J. FEINLEIB and W. PAUL: *Phys. Rev.*, **155**, 841 (1967).

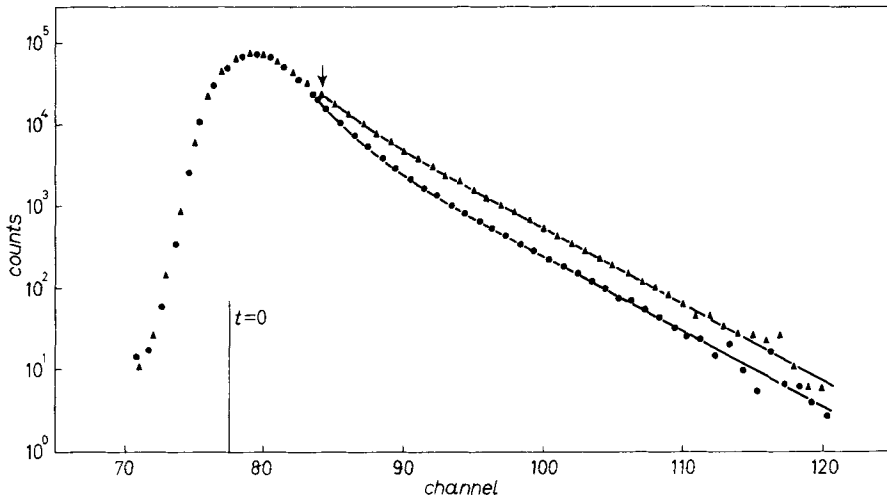


Fig. 2. - Measured positron decay curves in V_2O_3 at $T = 300^\circ K$ (upper curve) and at $T = 85^\circ K$ (lower curve). Both solid lines consist of two exponential decays as indicated in Figure. The arrow indicates the upper limit of the fit. 1 channel = $= 1.00 \cdot 10^{-10}$ s. \blacktriangle $\tau_1 = 2.01 \cdot 10^{-10}$ s, $\tau_2 = 4.75 \cdot 10^{-10}$ s, $I_2 = 48\%$; \bullet $\tau_1 = 1.97 \cdot 10^{-10}$ s, $\tau_2 = 4.97 \cdot 10^{-10}$ s, $I_2 = 21\%$.

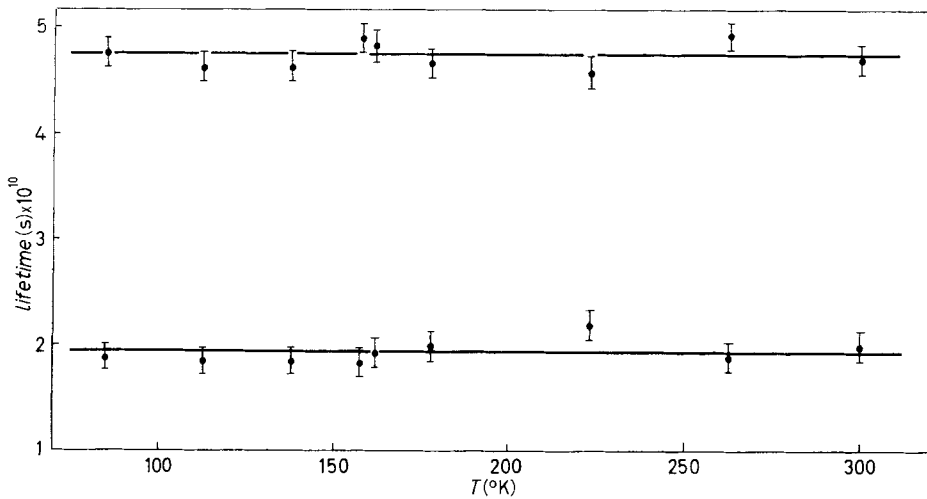


Fig. 3. - Positron lifetimes τ_1 and τ_2 vs. temperature in V_2O_3 . Upper curve $\tau_2 = (4.74 \pm 0.13) \cdot 10^{-10}$ s; lower curve $\tau_1 = (1.94 \pm 0.13) \cdot 10^{-10}$ s.

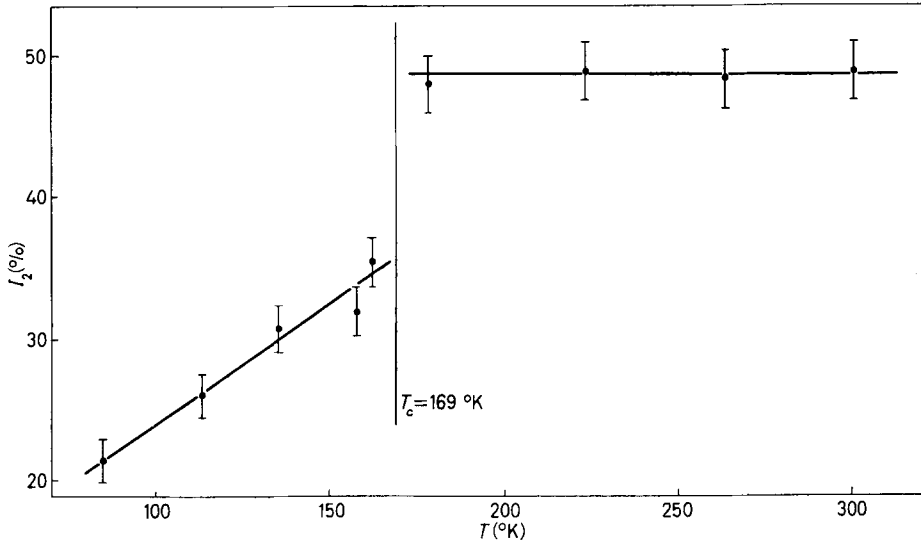


Fig. 4. - Observed temperature dependence of the intensity I_2 of the slower-decay component in V_2O_3 .

found in conductivity measurements cannot be evidenced. On the other hand, it does not seem particularly interesting to explore accurately the positron annihilation features near the critical temperature.

4. - Discussion.

The lifetime of slow positron in a medium with a nonuniform electron distribution is equal to the reciprocal of the spin-averaged decay rate λ (in units of s^{-1}) which can be given ⁽¹⁴⁾ by

$$\lambda = \pi r_0 c^2 \int_{\text{crystal}} \rho_+(\mathbf{r}) E(\mathbf{r}) \rho_-(\mathbf{r}) d\mathbf{r},$$

where $\rho_+(\mathbf{r})$ and $\rho_-(\mathbf{r})$ are respectively the positron and the electron charge distributions and $E(\mathbf{r})$ is a suitable enhancement factor which accounts for the electron-positron correlation.

Following the scheme outlined in the Introduction, $\rho_+(\mathbf{r})$ may be evaluated by solving the Schrödinger equation for the positron in the periodic potential of the lattice. This potential can be supposed to be nearly flat in metals and in covalent crystals such as the elements of the group IV, where the valence electrons are not strongly localized. In ionic crystals, however, where the valence

electron charge distribution is strongly nonuniform, the potential is presumably a strongly oscillating function and should give rise to positron energy states separated by one or even more energy gaps. The situation can be visualized in Fig. 5, where hypothetical one-dimensional positron bands are roughly shown for the case of a fundamental set of positron states separated by a gap from the continuous spectrum. Very small pockets of occupied states are also indicated, the occupation being controlled by a Boltzmann factor. The positron is slowed down to the bottom of its continuous spectrum by means of phonon excitations, and may then go down to the lower available energy states by means of radiative transitions.

We propose that this picture is realistic enough to ascribe the two lifetimes τ_1 and τ_2 observed, for example, in V_2O_3 to annihilations taking place from states lying respectively at the bottom of the fundamental band and of the continuous spectrum. Let these states be described by the wave functions ψ_1 and ψ_2 . Then ψ_1 turns out to be a more localized function than ψ_2 and is therefore supposed to give rise to the shorter lifetime τ_1 . It must be noted here that the whole argument is based on the hypothesis that the transition rate from the continuous to the lower states is comparable to the observed positron annihilation rates.

The probability that a positron be captured in lower states inside a ionic crystal may be roughly estimated by multiplying the time of collision, which in our case can be of the order of the observed positron lifetimes, with the capture rate by a single negative ion in free space. Unfortunately, calculations of the capture rate of a positron by an O^{--} ion have not been performed, data being available only for the H^-e^+ system (^{7,8}). In the latter case, this capture rate is strongly dependent on the particular bound state, but values of about $10^9 s^{-1}$ seem realistic enough thus giving rise inside the crystal to an easily observable capture probability.

Let us now discuss the effect of the transition to the metal state in V_2O_3 . The amount of the variation of the number of electrons in the conduction band does not appear to be univocally obtainable from electrical conductivity measurements. A strong change in mobility can in fact be associated with the resistivity jump. The theoretical treatment of ADLER and BROOKS (¹⁴), where the

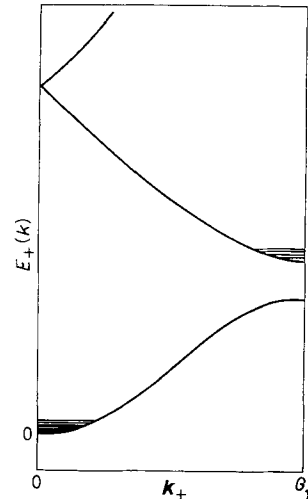


Fig. 5. - Hypothetical one-dimensional positron bands for the case of a fundamental set of positron states separated by a gap from the continuous spectrum.

(¹⁴) D. ADLER and H. BROOKS: *Phys. Rev.*, **155**, 826 (1967).

vanishing of the energy gap is assumed to be caused by the disappearance at T_c of the monocline distortion from rhomboedral symmetry, predicts that the carrier concentration will jump by a factor of 50 at the transition point. However, the qualitative behaviour of the carrier concentration is doubtlessly that of an exponential increase in the semi-conducting region, followed by a sudden jump to a constant value at the transition to the metal state. The conduction band is a narrow $3d$ sub-band, so that the conduction electrons may be considered as localized near the V^{3+} ions. The electron charge distribution in V_2O_3 is then strongly nonuniform even in the metal state and the most striking features of the positron band scheme are not greatly affected by the transition. The positron charge distribution presumably peaks near the O^{--} ions, the annihilation mainly taking place with the external electron shell of the oxygen ions. The increase in the concentration of conduction electrons then gives rise to a progressive increase of their screening effect only on the repulsive action of the V^{3+} ions, so that very small changes are expected with regards to the overlapping of $\rho_+(\mathbf{r})$ with the charge distribution of the O^{--} external electron shell. Moreover the changes in the enhancement factor $E(\mathbf{r})$ due to changes in the polarizability of the $3d$ electrons are confined to a space near the V^{3+} ions. Integrals like that given in the expression of λ are then expected to undergo very small changes when the temperature is varied, leading to the observed constancy of positron lifetimes in the explored temperature range. Finally the variations in τ_1 and τ_2 , which could be expected because of the 3.5% increase of the density in the transition to the rhomboedral symmetry⁽¹⁵⁾, are too low to be detected.

The increase of the screening effect on the repulsive action of the V^{3+} ions can be related to the observed increase in the intensity I_2 of the slower decay component. As per our main hypothesis, the intensities I_1 and I_2 are controlled by the positron transition rate from the bottom of the continuous spectrum to the fundamental band. This is merely the probability that the positron has of being captured in its lower-energy state corresponding to the more localized wave functions near the oxygen ions. One may reasonably assume that this capture rate decreases when the repulsive potential of the V^{3+} ions is gradually screened out by the presence of the conduction electrons. Thus, I_1 should decrease with temperature and I_2 , being complementary to I_1 , should increase with the same behaviour of the screening effect, that is, continuously in the semi-conducting region and with an abrupt jump at the transition point. This is what has been observed. In other words, we may say that when the repulsive potential of the V^{3+} ions is screened out, the positron spends a larger and larger fraction of its lifetime as a free positron.

(15) S. MINOMURA and H. NAGASAKI: *Journ. Phys. Soc. Japan*, **19**, 131 (1964).

5. - Conclusions.

a) The occurrence of a positron time-annihilation spectrum in V_2O_3 and, more generally, in ionic crystals is ascribed to annihilations taking place in different positron band states.

b) The observed constancy of positron lifetimes in the temperature range including the transition temperature to the metal state is explained in terms of localization of positron and electron wave functions.

c) The observed temperature dependence of the intensity of the slower-decay component may be ascribed to the screening effect of the conduction electrons on the repulsive action of the V^{3+} lattice ions.

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RIASSUNTO

Spettri temporali di decadimento dei positroni nel V_2O_3 sono stati registrati in un intervallo di temperature ($(80 \div 300)^\circ K$) comprendente la temperatura di transizione allo stato metallico. La comparsa di uno spettro di annichilazione complesso si suppone dovuta a positroni che occupano bande diverse. Si è trovato che le vite medie dei positroni $\tau_1 = 1.94 \cdot 10^{-10}$ s e $\tau_2 = 4.74 \cdot 10^{-10}$ s si mantengono costanti nell'intervallo di temperature esplorato. Ciò è stato spiegato considerando la localizzazione delle funzioni d'onda elettroniche e positroniche. Il comportamento con la temperatura delle intensità delle componenti di decadimento può essere assegnato all'effetto di schermo degli elettroni di conduzione sull'azione repulsiva degli ioni V^{3+} del reticolo.

Переход полупроводник-металл и аннигиляция позитрона в V_2O_3 .

Резюме (*). — Были измерены спектры времени жизни позитрона в V_2O_3 в области температур $(80 \div 300)^\circ K$, при которых имеет место переход в металлическое состояние. Наличие сложного спектра для времени аннигиляции позитрона приписывается аннигиляциям, которые происходят в различных позитронных зонных состояниях. Обнаружено, что времена жизни $\tau_1 = 1.94 \cdot 10^{-10}$ сек и $\tau_2 = 4.74 \cdot 10^{-10}$ сек являются постоянными в исследованной области температур. Это объясняется на основе локализации позитронных и электронных волновых функций. Обсуждается, что наблюдаемая зависимость от температуры интенсивностей компонент распада обусловлена эффектом экранирования электронов проводимости на основании отталкивания ионов решетки V^{3+} .

(*) *Переведено редакцией.*