

Positron Annihilation with Valence Electrons in Th_3As_4 and U_3As_4

B. ROZENFELD AND E. DĘBOWSKA

Institute of Experimental Physics, University of Wrocław, Wrocław, Poland

AND Z. HENKIE

Institute for Low Temperature and Structure Research, Polish Academy of Sciences, Wrocław, Poland

Received September 30, 1974; in revised form, August 19, 1975

The angular distributions of annihilation photons (ADAP) for polycrystalline samples of the nonmagnetic semiconductor Th_3As_4 and the magnetically-ordered-at-lower-temperatures, semi-metallic U_3As_4 are compared. The "tail" component (high-angle part) in the ADAP curve for U_3As_4 , markedly higher than for Th_3As_4 , is thought to be the result of annihilation with $5f$ electrons being localized at the uranium ionic core. The number of valence electrons per molecule calculated in the free-electron model approximation from the small-angle part of the ADAP curve is equal to 31.7 ± 1.4 for Th_3As_4 and 32.7 ± 1.4 for U_3As_4 .

Introduction

Most of the uranium pnictides crystallize in one of the following three types of structure: $\text{NaCl}(\text{UX})$, anti- $\text{Cu}_2\text{Sb}(\text{UX}_2)$, and Th_3P_4 (U_3X_4). All of them show an electrical conductivity of metallic character, and magnetic ordering at low temperatures (1-5). Assuming a localized character of the $5f$ electrons in the NaCl type of uranium pnictides and chalcogenides as well as using the RKKY theory it was possible to calculate the correct ranges of stability of ferro- and antiferromagnetic ordering (6). The calculations of the electronic structure (7) showed that in these compounds the Fermi level intersects the hybridized f - d bands. An attempt at explanation of experimental magnetic data was made for all three types of uranium pnictides by assuming in the calculations that the $5f$ electrons have a somewhat itinerant character (8). In this work the investigation of electron positron annihilation in U_3As_4 has been used to determine a character of $5f$ electrons.

The examination of positron-electron annihilation in a substance by determining the

angular distribution of annihilation photons (ADAP) is one of the methods which allows us to obtain direct information about its electronic structure. A lot of information about this method can be found in Dekhtyar's (9) review on the use of positron annihilation for the study of solids.

Many factors may have an effect on the ADAP curve and the interpretation of the positron annihilation data is sometimes difficult, especially in complex substances. For this reason, it is important to compare the ADAP curves for uranium compounds with those for simple isostructural compounds. This is why U_3As_4 and Th_3As_4 have been chosen for investigation. The latter compound is a nonmagnetic semiconductor (10, 11).

Experimental

The ADAP curves for polycrystalline samples of Th_3As_4 and U_3As_4 at room temperature were determined by means of a standard scintillation spectrometer (12) using a 10 mCi ^{22}Na source on one side of the sample. The fwhm of the horizontal resolving

power of the apparatus was about 0.8×10^{-3} radians.

The samples were in the form of long strips about 8 mm wide and 1 mm thick. The U_3As_4 sample was obtained by the chemical transport method (13). The residual resistivity ratio, $R_{300}/R_{4.2}$, the parameter usually used to characterize purity of metallic conducting samples, is equal to 250. The Th_3As_4 was prepared by the diffusion of As atoms into a thin slab of metallic thorium for 6 weeks (11). The sample obtained by this method had a carrier concentration equal to $2.1 \times 10^{18} \text{ cm}^{-3}$ and consists of crystallites of the same order as the U_3As_4 sample. Hence, we expect the same order of defect concentration in samples of both compounds despite different methods used to obtain them.

Results and Discussion

The experimental ADAP curves without background are presented in Fig. 1. The coincidence counting rate $N(\theta)$ has been normalized by fitting the ADAP curve to unity for the angle $\theta = 0$.

For some metals the $N(\theta)$ curve has the shape of a reversed parabola at small θ , and this parabola transforms into a gaussian curve for larger angles ("tail" component). According to the (9), this shape may be described by the equation:

$$\begin{aligned} N(\theta) &= N_v(\theta) + N_c(\theta) \\ &= 2A(\theta_F^2 - \theta^2)f(|\theta_F| - |\theta|) \\ &\quad + B \exp(-\theta^2/C) \end{aligned} \quad (1)$$

where θ is the angle of deviation from the collinearity of annihilation photons, and $\theta = p_z/mc$. Further,

$$\begin{aligned} f(|\theta_F| - |\theta|) &= 1 & \text{for } |\theta| < |\theta_F| \\ &= 0 & \text{for } |\theta| > |\theta_F|. \end{aligned}$$

p_z is the z th momentum component of the annihilating electron, and θ_F refers to the Fermi momentum. A and B are normalization constants. The $N_v(\theta)$ part is connected with positron-valence electron annihilation and $N_c(\theta)$ with core annihilation; hence, C is a constant depending on the penetration depth

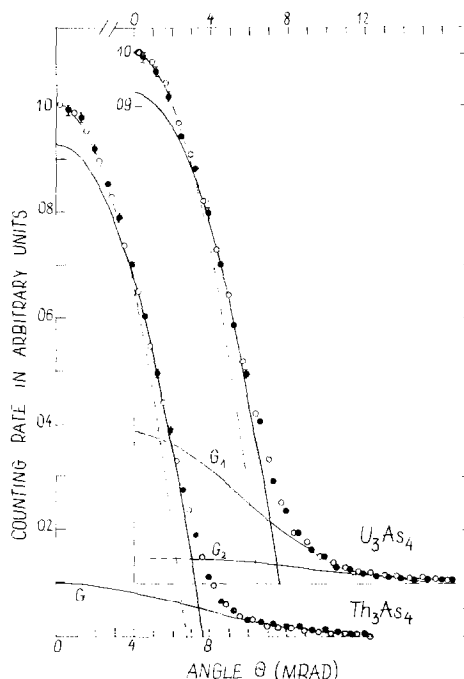


FIG. 1. Angular distributions $N(\theta)$ of annihilation photons (ADAP) for Th_3As_4 and U_3As_4 . Solid and open points present the $N(\theta)$ data for $+\theta$ and $-\theta$, respectively.

of the positron wavefunction into the ionic core.

The $N(\theta)$ curves for the polycrystalline Th_3As_4 and U_3As_4 have very similar shape to each other at small angles θ , and both may be fairly well approximated by two reversed parabolas, as shown in Fig. 1. On the other hand, there are some differences in the magnitude and shape of curves of the "tail" components. The "tail" component is bigger for U_3As_4 than for Th_3As_4 . For $\theta > 9.5$ mrad, the experimental data of $N(\theta)$ for Th_3As_4 yield one straight line in the $(\ln N(\theta), \theta^2)$ plot and the tail component is approximated by the gaussian curve G presented in Fig. 1. In the similar plot for U_3As_4 the $N(\theta)$ data follow two straight lines in two ranges of θ values. Two gaussian curves G_1 and G_2 fitted to experimental data of $N(\theta)$ in these two ranges are presented in Fig. 1 to illustrate differences in shape and magnitude of "tail" components of Th_3As_4 and U_3As_4 . The G_1 curve only was taken as a distribution of core annihilation

rate. Some enhancement in the "tail" part of the ADAP curve may be due to higher momentum components in the conduction electron wavefunctions and electron-positron correlation. It seems, however, that the large difference in the "tail" components of both compounds is mostly due to the increased annihilation with core electrons of U₃As₄ in respect to that of Th₃As₄. This conclusion combined with the fact that uranium atom has two 5*f* electrons more than thorium speaks in favor of a localized character of these electrons in U₃As₄.

The estimation of the maximum value of the core electron momentum on the basis of the "tail" part of the $N(\theta)$ curve is not possible. But there is some interest in the quantitative evaluation of the ratio W of the contribution to the annihilation process of both valence and ionic core electrons (14), defined as the ratio of the area S_p under the parabolic part of the $N(\theta)$ curve to the area S_g under the gaussian: $W = S_p/S_g$. The W value in the paper (14) was calculated in a somewhat different way, but this does not change the conclusion. The W ratio for Th₃As₄ and U₃As₄ is significantly different and equal to 4.9 and 1.8, respectively, while the W ratio for the first three polycrystalline hexagonal rare earths (La, Pr, Nd): (15) is nearly constant. In the latter case the W ratio markedly differs from that for the other hexagonal rare earths (Gd, Tb, Dy, Ho). It means that W value depends not only on the number of localized f electrons, but also on their interaction with conductivity electrons. The localized character of 5*f* electrons in U₃As₄ was previously confirmed on the basis of studies of the Hall effect, which revealed a proportionality between the spontaneous Hall constant and the spin-disorder resistivity (16). The anomalous Hall constant is 4 orders higher than the ordinary Hall constant. This can mean that strong interaction between localized and conductivity electrons exists and that the strong difference in the W value observed in the examined compounds also may be due to this strong interaction.

On the basis of the distribution of the z th momentum component, we can find the distribution of the absolute momentum value $N(p)$, and the momentum density distribution

$\rho(p)$ of the valence electrons. For polycrystalline samples, Stewart's formulas may be applied (17)

$$N(p) dp \sim -2p \left(\frac{dN(p_z)}{dp_z} \right)_{p_z=p} dp \quad (2a)$$

$$\rho(p) dp \sim \frac{1}{2p} \left(\frac{dN(p_z)}{dp_z} \right)_{p_z=p} dp. \quad (2b)$$

The $N(p)$ and $\rho(p)$ dependences for both measured compounds, calculated according to Eq. (2), are presented in Fig. 2. The derivatives dN/dp of the valence electron part of ADAP curve $N_v(\theta)$ has been computed from the algebraic expressions of the parabolas in the ranges of the overlap of the parabolas and experimental data. In the other ranges, the graphical differentiation has been used. The separation of the conduction electron parts from the ADAP curves has been reached by using the gaussian curves $G(\text{Th}_3\text{As}_4)$ and $G_1(\text{U}_3\text{As}_4)$ as the core electron parts. The momentum p_{max} corresponding to the maximum of the distribution $N(p)$ represents the Fermi momentum in a simple free-electron model. Because of the finite resolution of the

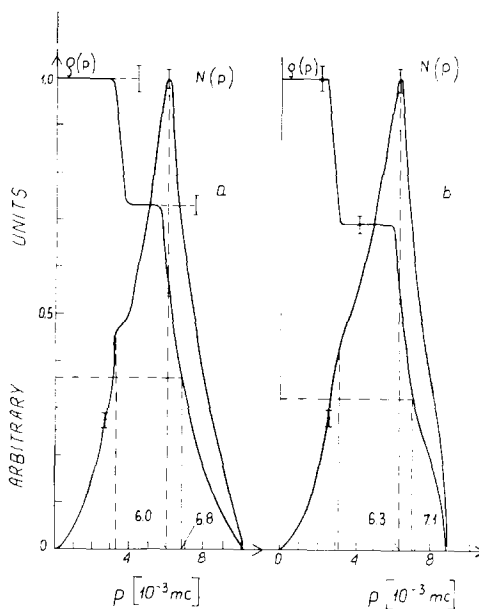


FIG. 2. Distributions of the momentum absolute value $N(p)$ and momentum density distributions $\rho(p)$ for Th₃As₄ (a) and U₃As₄ (b).

measuring device the value of p_{\max} must be corrected (12):

$$p_F = p_{\max} + 0.8 \times 10^{-3} \text{ mc.} \quad (3)$$

The Fermi momenta determined in this way for Th_3As_4 and U_3As_4 are 6.8×10^{-3} mc and 7.1×10^{-3} mc, respectively. These values are in agreement with p_F obtained from the fwhm of the $\rho(p)$ distributions.

The number z of valence electrons per molecule for the free-electron model is calculated from p_F according to the relation (12):

$$z = \frac{8}{3h^3} \frac{M}{dL} p_F^3 \quad (4)$$

where M is the molecular mass, d is the density, and L is the Avogadro number, or

$$z = 9.7 \times 10^{-4} \frac{M}{d} p_F^3 \quad (4a)$$

where d is given in g/cm^3 , and p_F is given in 10^{-3} mc.

As follows from Eq. (4a), the number of valence electrons per molecule is equal to 31.7 ± 1.4 and 32.7 ± 1.4 for Th_3As_4 and U_3As_4 , respectively.

From the plateau on the $\rho(p)$ curves it may be concluded that in both compounds, the valence electrons are divided into two groups corresponding to two reversed parabolas constituting the $N(\theta)$ curves. The number of electrons per molecule in the first group is equal to 8.0 ± 0.4 in Th_3As_4 and 6.4 ± 0.4 in U_3As_4 , and is calculated for the momentum value corresponding to the expected first maximum of $N(p)$ curves. As this maximum cannot be precisely determined from $N(p)$ curve, the point of intersection of the parabolas was taken as a point corresponding to this maximum.

The above simplified method used in the analysis of the ADAP curves for both uranium and thorium arsenides has given helpful information about the electronic structure of transition metals and alloys (9, 12, 14). There is a lack of information about the use of this method in semiconducting compounds, but for semiconducting elements, e.g., Si and Ge (18), the $N_v(\theta)$ part of the ADAP curves is well

describable by the free-electron model. Weisberg and Berko (19) have found the same positron lifetime in intrinsic and heavily n -type Ge and Si. This lifetime is short, as in metals, thanks to a high concentration of valence electrons. High and almost the same concentration of the valence electron in both compounds under examination justifies the same treatment of the ADAP curves though Th_3As_4 is a semiconductor and U_3As_4 is a semimetal.

Electrostatic energy and valence band considerations in the Th_3P_4 structure allowed Carter (20) to expect a covalent valence of 4 for Th and 3 for P as well as the semiconducting character of the stoichiometric compound. This conclusion is true for Th_3As_4 , which turned out to be a semiconductor with the forbidden energy gap $E_0 = 0.29$ eV (11), but it is not true for U_3As_4 which shows metallic conductivity with a carrier concentration larger than $1.2 \times 10^{22} \text{ cm}^{-3}$ (16). On the basis of Carter's (20) considerations we expect that the 32 valence electrons of Th (3×4) and As (4×5) are in Th_3As_4 divided into two groups. One of them contains 24 electrons which take part in the formation of the covalent bonding. The symmetry of Th_3As_4 requires hybridized bonding orbitals of only p and d character. The participation of those electrons in the covalent bonding causes an increase of their p momenta. The other group with lower p momenta contains the eight remaining electrons of As (4×2).

Within the experimental error limit, the number of valence electrons in U_3As_4 agrees with the number of 32 valence electrons in the Th_3As_4 case, though the uranium atom has two $5f$ electrons which are absent in thorium. There is, however, a small change in the distribution of these 32 valence electrons in U_3As_4 in comparison to that in Th_3As_4 . The group of electrons with the smaller momenta consists here of only 6.4 ± 0.4 electrons per molecule, while in Th_3As_4 it consists of 8 electrons per molecule. It is possible that the above difference results from the change of the chemical bonding and is responsible for the metallic character of the electrical conductivity of U_3As_4 , in contrast to the semiconducting properties of Th_3As_4 .

From the above analysis of the $N_p(\theta)$ part of the $N(\theta)$ curves for U₃As₄ we expect that the additional six $5f$ electrons per molecule are localized at the uranium ionic core, giving an increase of the "tail" component of the ADAP curve for U₃As₄ compared to that for Th₃As₄. Such behavior of the $5f$ electrons of uranium in U₃As₄ differs strongly from that in metallic uranium.

The positron annihilation study of metallic thorium and uranium (21) by the same method has given 4 and 6 valence electron per atom, respectively. The 6 valence electrons per atom in metallic uranium are divided into two groups, 1.9 ± 0.2 and 4.1 ± 0.4 electrons, corresponding to the two reversed parabolas on the $N(\theta)$ curve. These data were interpreted in terms of the hybridization of f - d bands. This result is in agreement with the calculations of the electronic structure of metallic uranium (22).

Acknowledgments

The authors would like to express their thanks to Prof. W. Trzebiatowski for his kind interest in this work and to Dr. H. Stachowiak and Dr. J. Mulak for helpful discussions.

References

1. I. H. WARREN AND C. E. PRICE, *Canad. Met. Quart.* **3**, 183 (1964).
2. I. H. WARREN AND C. E. PRICE, *Canad. Met. Quart.* **3**, 245 (1964).
3. Z. HENKIE AND C. BAZAN, *Phys. Status Solidi (a)* **5**, 259 (1971).
4. Z. HENKIE AND Z. KLETOWSKI, *Acta Phys. Polon.* **A42**, 405 (1972).
5. W. TRZEBIATOWSKI, "Magnetismus," p. 88, Leipzig (1967).
6. J. GRUNZWEIG-GENOSSAR, M. KUZNIETZ, AND F. FRIEDMAN, *Phys. Rev.* **173**, 562 (1968).
7. H. L. DAVIS, "Lectures of the XIth Winter School of Theoretical Physics," Karpacz (1974).
8. H. ADACHI AND S. IMOTO, *J. Phys. Chem. Solids* **34**, 1537 (1973).
9. I. YA. DEKHTYAR, *Phys. Letters* **9C**, 243 (1974).
10. I. H. WARREN AND C. E. PRICE, *Advanced Energy Conversion* **4**, 169 (1964).
11. Z. HENKIE AND P. J. MARKOWSKI, to appear.
12. B. ROZENFELD, *Acta Phys. Polon.* **31**, 197 (1967).
13. Z. HENKIE, *Roczniki Chemii* **42**, 363 (1968).
14. B. ROZENFELD, M. SZUSZKIEWICZ, AND W. WIERZCHOWSKI, *Acta Phys. Polon.* **A40**, 3 (1971).
15. S. SZUSZKIEWICZ, *Acta Phys. Polon.* **A44**, 691 (1973).
16. Z. HENKIE, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* **20**, 531 (1972).
17. A. T. STEWART, *Canad. J. Phys.* **35**, 168 (1957).
18. J. C. ERSKINE AND J. D. MCGERVEY, *Phys. Rev.* **151**, 615 (1966).
19. H. WEISBERG AND S. BERKO, *Phys. Rev.* **154**, 249 (1967).
20. F. L. CARTER, "Rare Earth Research" (L. Eyring, Ed.), Vol. III, Gordon Breach, New York/London (1965).
21. B. ROZENFELD AND M. SZUSZKIEWICZ, *Nukleonika* **11**, 693 (1966).
22. E. A. KMETKO AND H. H. HILL, *Nucl. Met.* **17**, 233 (1970).