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POSITRON ANNIHILATION IN SEMIMETALLIC UX_2 AND $UAsY$ COMPOUNDS (X = P, As, Sb, AND Y = S, Se, Te)

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The angular distribution of annihilation quanta (ADAQ) was determined for single crystals and polycrystalline samples of UX_2(X = P, As, Sb) and $UAsY$(Y = S, Se, Te) compounds. Both groups of compounds show directional anisotropy of ADAQ curves which is greater for UX_2 compounds. The number of valence electrons per molecule was calculated in the free-electron model approximation from ADAQ curves for polycrystalline samples. It is smaller than the sum of valence electrons of constituent elements for all examined compounds. The differences between ADAQ for both UX_2 and $UAsY$ compounds are discussed on the basis of possible fulfillment of the Brillouin zones constructed for the simplified structures of these compounds.

1. Introduction

Detailed determination of the electronic structure by the positron annihilation method requires comparison of the experimental angular distribution of annihilation quanta (ADAQ) curves with the theoretical ones obtained on the basis of adequate electron and positron wave functions and postulated Fermi surface shape. The situation is more complicated for compounds of unknown band structure since the chemical bonding character is not completely explained. In these cases investigation of the series of compounds for which a systematic change of chemical bonding may be expected is preferable. The usefulness of this approach has been recently shown for thorium and uranium arsenides with Th_3P_4 structure [1]. Th_3As_4 is a nonmagnetic semiconductor with well defined covalent bonding. The analysis of ADAQ curves based on the free-electron model approximation has revealed 32 valence electrons per molecule among which 24 electrons take part in covalent bonding.

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The comparison of ADAQ curves for Th_3As_4 and U_3As_4 has allowed us to come to the conclusion that the electrons of uranium are localized at the ionic core. The number of valence electrons in U_3As_4 agrees with 32 electrons for Th_3As_4 but one observes a small change in their distribution into two groups. This may result from the change in the chemical bonding and is consistent with the metallic character of electric conductivity of U_3As_4.

The purpose of this paper is to present ADAQ curves for uranium compounds UX_2 (X = P, As, Sb) and UAsY (Y = S, Se, Te) and settlement of assumptions for the next Fermi surface details calculations.

The compounds under investigation crystallize in P4/n mm tetragonal system [2–4] except for UAsTe [7, 8] which displays I4/m mm structure and UP_2 below 356 K, where the existence of a superlattice is observed, and the space group is I4 m m [5, 6]. UX_2 compounds are at low temperature uniaxial collinear antiferromagnets [9–11] with the magnetic moments parallel to the c-axis, whereas UAsY compounds are uniaxial collinear strongly anisotropic ferromagnets [12–14] with the anisotropic constants of the order of $6\text{–}10 \times 10^6$ erg/Gs.

Both UX_2 [15–17] and UAsY [18] compounds show very large anisotropy of the electric transport properties. At room temperature the ratio of the thermoelectric power in the direction perpendicular to the c-axis and along the c-axis is equal to 1.7–1.3 for UX_2 [17] and equal to 7–3 for UAsY [18] compounds; in all cases thermoelectric power has a positive sign. For UP_2 [15] the electric resistivity along the c-axis is more than three times larger than in the perpendicular direction, which indicates that different electron scattering conditions exist along these directions.

2. Experimental part

The ADAQ curves for polycrystalline and single crystal samples of examined compounds were determined at room temperature with the conventional parallel slit annihilation spectrometer [19] using a 10 mCi ^{22}Na source placed on one side of the sample. The horizontal angular resolving power of the apparatus was about 0.8×10^{-3} rad.

The polycrystalline samples were prepared by pressing powdered compounds into the form of slabs with dimentions $17 \times 8 \times 1$ mm^3. The crystals have been grown by the chemical transport method [20] in the form of a plate perpendicular to the [001] direction, and samples for measurement were prepared from a few such plates to extend radiated surface up to dimensions similar to polycrystalline samples.

The measurements along [011] and [111] directions were performed by appropriate orientation of the sample in the apparatus, however, it made the resolving power of the spectrometer somewhat worse. Because of the small dimensions of UAs_2 crystals for this compound the measurements have been made for polycrystalline samples only.

3. Results and discussion

Experimental ADAQ curves $N(\theta)$ normalized to the same area are shown in Fig. 1. The characteristic feature of the "tail" part of every curve for polycrystalline samples is the possibility of two gaussians fitting the experimental points, as was observed for U_3As_4.

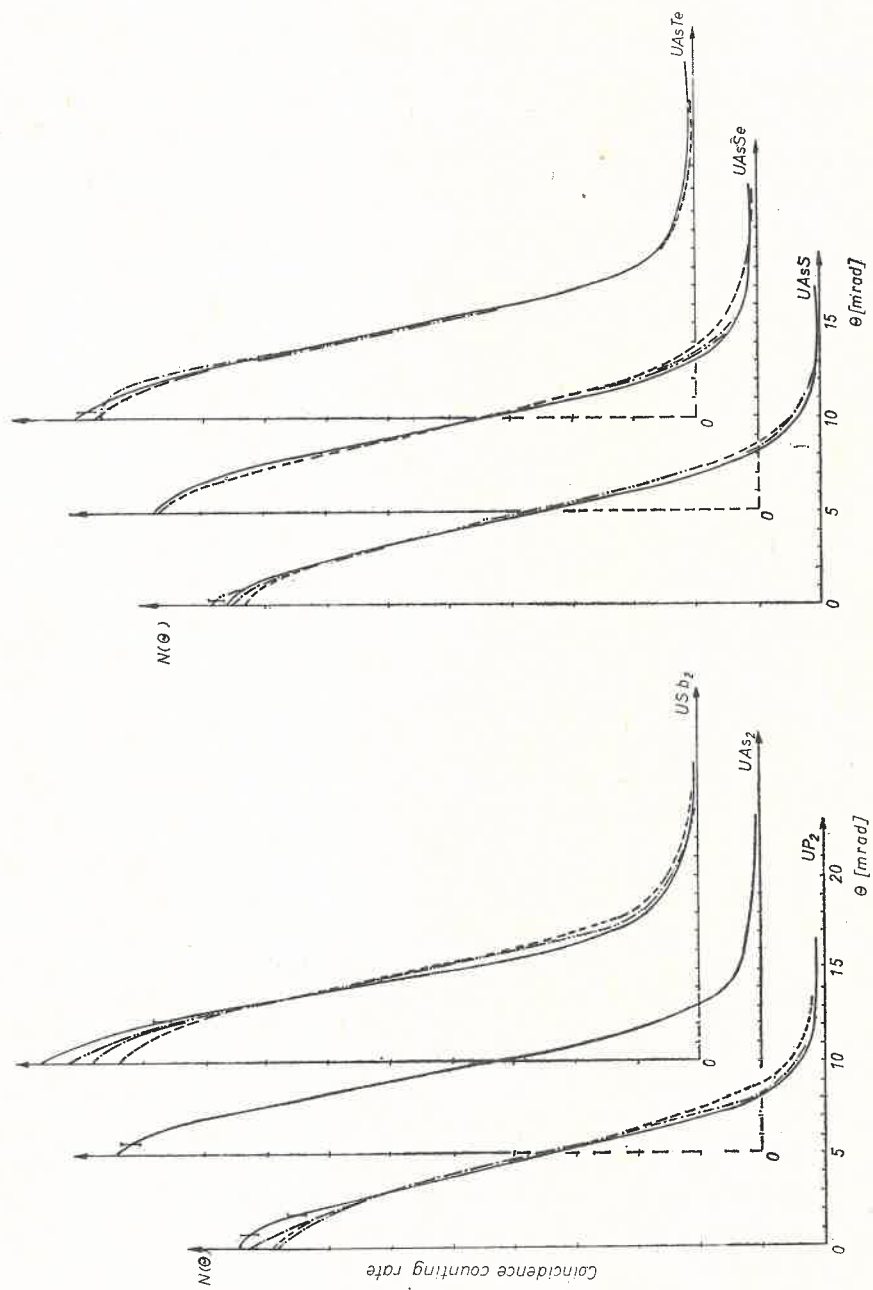

Fig. 1. Experimental ADAQ curves $N(\theta)$ normalized to the same area

Because the distances between U — U atoms in these compounds are not smaller than in U_3X_4 [21], the f — electrons ($5f^2$ as magnetic data suggest) are supposed to be localized at the uranium ions and contribute to the "tail" part of ADAQ curve as was found for U_3As_4.

Experimental points after subtraction core annihilation may be best approximated by two reversed parabolas, which indicates the valence electrons division into two groups of electrons. The first electron group with smaller maximum momenta p_c is thought to be responsible for the metallic character of the electric conductivity and the second one contains electrons participating in chemical bonding of covalent or ionic character. Let us denote the maximum momentum of all valence electrons by p_v.

The p_c and p_v momenta values determined from $\varrho(p)$ curves (Fig. 2) obtained according to Stewart [22] and corresponding number of electrons Z_c and Z_v in the free electron

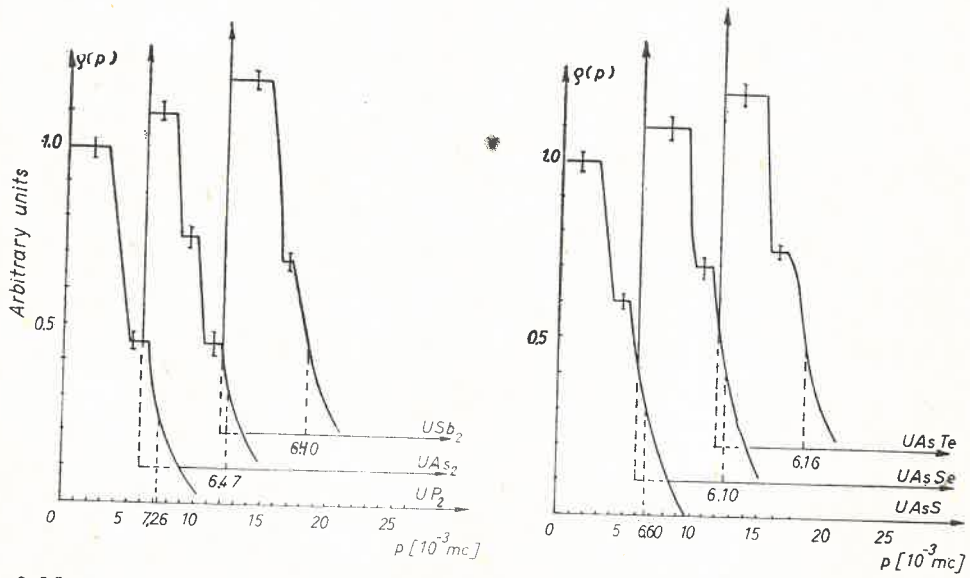

Fig. 2. Momentum density distribution $\varrho(p)$ obtained on the basis of ADAQ curves after eliminating core annihilation

model approximation are collected in Table I. Z_v values are, within the limit of experimental error, equal to 10 or 12; so in all cases they are smaller than the sum of all valence electrons (without $5f^2$ electrons), which are 14 and 15 for UX_2 and UAsY respectively. It is possible that these electrons are not "seen" by the positron to the same extent. Investigation of the electronic structure of Sb by the ADAQ method [23] has led the author to the suggestion, that the number of collectivized electrons in this element in a crystal form is smaller than 5 (as one may expect) and is equal to 3.8 ± 0.2. There is a possibility that this feature also manifests itself in antimony compounds and is responsible for the number $Z_v = 12.2 \pm 0.4$ electrons per molecule in USb_2. There is a lack of information about valence electrons in As, but in Se and Te [24] the anticipated number of 6 electrons

TABLE I

Compound	$p_v 10^{-3}$ mc	Z_v	$p_c 10^{-3}$ mc	Z_c
UP_2	7.26±0.13	12.6±0.4	3.9±0.4	2.0±0.4
UAs_2	6.47±0.13	10.0±0.4	4.2±0.4	2.8±0.4
USb_2	6.40±0.13	12.2±0.4	3.8±0.4	2.5±0.4
UAsS	6.60±0.13	10.3±0.4	3.3±0.4	1.3±0.4
UAsSe	6.40±0.13	10.1±0.4	3.4±0.4	1.6±0.4
UAsTe	6.46±0.13	11.7±0.4	3.3±0.4	1.5±0.4

p_v — momentum of valence electrons fixed at FWHM of the momentum density distribution; p_c — momentum of conduction electrons fixed at the point of intersection of two parabolas fitted to the experimental points; Z_v — number of valence electrons; Z_c — number of conduction electrons.

per atom has been found. The numbers Z_c electrons per molecule are for UX_2 greater than 2 and for UAsY greater than 1, which corresponds to the more ionic character of chemical bonding in UAsY, resulting from the greater difference in electronegativity of the components as compared to UX_2.

We have mentioned the very large anisotropy of electric resistivity and different electron scattering conditions along the c-axis and a-axis due to some layer character of the structure of these compounds. The predominant part of the resistivity constitutes the so-called spin-disorder resistivity which is nearly constant in the paramagnetic range,

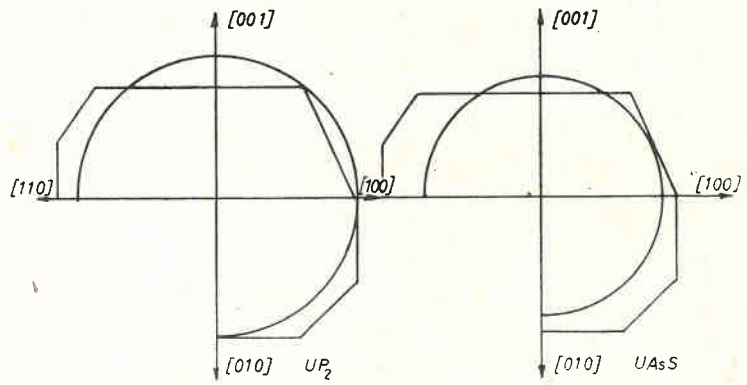

Fig. 3. Conduction electron spheres (with radius p_c) on the background of the Brillouin zone section in different planes for UP_2 and UAsS

caused by a conduction electron interacting with a localized $5f^2$ electron. So, in the first approximation, scattering potential may be thought to have the same lattice periodicity as uranium atoms, and only this lattice could be taken into account in constructing the reciprocal lattice and Brillouin's zones in $\vec{k}$ — vector space. If one neglects about 6 per cent

distortion of uranium atom from the center of unit-cell along the fourfold axis the uranium atoms display bct Bravais lattice. The first Brillouin zone (BZ) for such a simplified lattice is filled by 2 electrons per molecule for all examined compounds. For UAsY the number Z_c of free electrons per molecule is equal to about 1, then only half of the states in BZ should be occupied and Fermi surface (FS) is supposed to be nearly spherical. On the other hand more than 2 free electrons per molecule in UX_2 should cause passage of the FS to the second BZ especially in [001] direction because of the smallest distances to the Brillouin zone boundary in this direction. Because of some layer character of the structure we expect an energy gap at this boundary which is not large enough to prevent the occupation of electronic states in the second zone but quite enough to prefer occupation of electronic states of first BZ. In this case FS may be very distorted from the spherical shape. In Fig. 3 there are examplary spheres with radii p_c against the background of the different Brillouin zone sections for UP_2 and UAsS, and the difference in the electron occupation of momentum states for these compounds is evident. These qualitative evaluations are in agreement with the observed profiles of ADAQ curves, their anisotropy for different crystallographic directions is more for UX_2 than for UAsY (Fig. 1) due to more complicated FS shape in UX_2 compounds.

The concentration of conduction electrons in UP_2 [20] estimated from the ordinary Hall coefficient with assumption of only one kind of carrier is equal to 1.1 per molecule and is consistent with our calculation according to the present knowledge of band structure. This confirms the unsefulness of the proposed model which also allows one to interpret, in a simple way, the experimental results we have obtained hitertho.

The qualitative characteristics presented in this paper are the basis for further calculations of absolute momentum distributions and Fermi surface shape details, on the ground of ADAQ curves for oriented single crystals.

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