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## Positron lifetime in non-stoichiometric carbides with a B1(NaCl) structure

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**Abstract.** The positron lifetimes in the carbides of the tetravalent group IV transition metals are found to be similar to those in the corresponding pure metals whereas in the carbides of the pentavalent group V metals the positron lifetimes are by about 40 ps longer than in the pure metals. A representation of the positron annihilation rate versus the density of metal valence electrons demonstrates that the positrons are predominantly annihilated with metal valence electrons in these carbides. This result is strongly supported by the decrease of the positron lifetime in  $NbC_y$  with carbon vacancy content  $1 - y$  and is interpreted as positron annihilation on vacant sites of the carbon sublattice.

### 1. Introduction

The carbides of the group IV and group V transition metals are characterized by a wide range of existence of the rock-salt (B1) crystal structure so that these materials  $MC_y$  may be stable even at large deviations  $1 - y$  from the stoichiometric composition  $MC_{1.00}$  giving rise to high densities of structural vacancies on the carbon sublattice [1]. Upon insertion of carbon atoms ( $y > 0.5$ ) the HCP lattice of the group IV metals and ( $y > 0.7$ ) the BCC lattice of the group V metals are transformed into the FCC metal sublattice of the carbides with the carbon atoms occupying octahedral interstitial sites.

The presence of structural vacancies affects the properties of the compounds via their electron and phonon characteristics. Interaction of vacancies and ordering in the carbon sublattice leads to additional modifications of the macroscopic solid-state properties [2].

Positron lifetime studies have proved a sensitive technique for investigating vacancies in metals [3,4], semiconductors [5], and metal oxides [6] and for testing changes in the electronic densities, e.g., between metals and their oxides [7]. In the present study we compare positron lifetime data on group IV and group V transition-metal carbides with those from the corresponding pure metals and report positron lifetime measurements on  $NbC_y$  as a function of composition  $y$  in order to investigate whether positrons are annihilated with metal valence electrons.

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## 2. Experimental procedure

In order to investigate whether the 'free' delocalized positron state in transition metal carbides TiC, ZrC, HfC, NbC, and TaC can be observed, specimens with carbon contents as near to the stoichiometric composition as possible were prepared. The maximum carbon contents  $y_{\max}$  in accordance with [1] are shown in table 1. For studying the effect of deviations from the stoichiometric composition in NbC<sub>y</sub>, additional specimens were prepared in the wide homogeneity region  $0.72 < y < 1.00$  of the cubic B1 phase. The NbC<sub>y</sub> system has been well studied by means of structural, magnetic and thermal techniques [2].

**Table 1.** Maximum carbon contents  $y_{\max}$ , cubic lattice parameters  $a_{B1}$ , and positron lifetimes  $\tau_{MC_y}$  of group IV and group V metal carbides and 'free' positron lifetimes  $\tau_M^f$  in the corresponding pure metals. Experimental errors of  $\tau$  are  $\pm 1$  ps.

	TiC <sub>y</sub>	ZrC <sub>y</sub>	HfC <sub>y</sub>	NbC <sub>y</sub>	TaC <sub>y</sub>
$y_{\max}$	1.00	0.98	1.00	1.00	0.99
$a_{B1}$ (Å)	4.328	4.698	4.639	4.470	4.456
$\tau_{MC_y}$ (ps)	160	176	173	161	155
$\tau_M^f$ (ps)	147	165	174	119	116

The carbide specimens were synthesized by reacting metal together with carbon powders in a vacuum of  $1.3 \times 10^{-3}$  Pa at temperatures between 2000 and 2500 K for 15 to 20 h with subsequent cooling to ambient temperature within 3 h. This technique provides large grains (4–8  $\mu\text{m}$ ) in the polycrystalline specimens. Therefore positron annihilation in the grain boundaries can be neglected. With x-ray diffraction studies a homogeneous macroscopic distribution of carbon and the cubic crystal structure with the lattice parameters given in table 1 were detected.

For the present investigations the sintered metal carbides were cut into  $8 \times 8 \text{ mm}^2$  specimens with a thickness of 1 mm for TiC, 0.5 mm for ZrC and NbC, and 0.3 mm for HfC and TaC, and were given a final mechanical polishing.

For the positron lifetime measurements a  $^{22}\text{NaCl}$  positron source was deposited on Al foil (thickness 0.8  $\mu\text{m}$ ) which was sandwiched between two specimen platelets. The lifetime measurements were performed by means of a conventional fast-slow  $\gamma\gamma$  spectrometer equipped with BaF<sub>2</sub> scintillators and with a time resolution FWHM of 230 ps. The positron lifetime spectra (time channel width 12.2 ps) with about  $2.5 \times 10^6$  total coincidence counts were numerically evaluated by multicomponent fits [8]. The intensity and time constant of a source contribution were determined to about 5% and 350 ps, respectively.

## 3. Experimental results and discussion

The positron lifetimes in metal carbides  $\tau_{MC_y}$  with compositions close to stoichiometry as well as the free positron lifetimes  $\tau_M^f$  in the corresponding metals [3, 9] are shown in table 1. The positron lifetimes 160 to 176 ps measured in the group IV metal carbides differ only slightly from those in the pure metals whereas the values 155 to 161 ps in the group V metal carbides are about 40 ps longer than in pure Ta or

Nb. In  $\text{NbC}_y$  the positron lifetime decreases from 161 ps to 151 ps when the carbon content is decreased from  $y = 1.00$  to  $y = 0.72$ .

In order to discuss the present data we consider the normalized positron annihilation rate

$$\lambda^* = (\lambda - \lambda_\infty) / \lambda_\infty$$

and the normalized density of electrons

$$\eta = ZV_B/V$$

where  $\lambda = 1/\tau$  or  $\lambda_\infty = 2.004 \times 10^9 \text{ s}^{-1}$  denote the positron annihilation rates measured in the solid or expected for the 'low-electron density' spin-averaged limit, respectively. The quantity  $Z$  denotes the number of electrons in one formula unit with the volume  $V$ ; Bohr's hydrogen volume  $V_B = 6.208 \times 10^{-31} \text{ m}^3$  is used for normalization.

For metals the relationship

$$\lambda^* = (24.8\eta)^{0.81} \quad (1)$$

was derived [10] where  $\eta$  is the valence electron density. For metal oxides this relationship is invalid because core electrons and different electronic screening of the positron charge play an essential role in positron annihilation in insulators [11]. Schaefer and Forster [7] showed that for the oxides  $\text{ZrO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{NiO}$ , and  $\text{MgO}$  the changes

$$\Delta\lambda^* = 0.096 + 2.2\Delta\eta^{\text{tot}} \quad (2)$$

of the normalized annihilation rate between the metal oxides and the corresponding pure metals are linearly related to the changes  $\Delta\eta^{\text{tot}}$  of the total electron densities between metal oxides and the corresponding pure metals.

The present positron annihilation rates in metal carbides can be correlated neither to the valence electron densities, as in metals [10], nor to the total electron densities, as in metal oxides [7]. This may originate from the structural and electrical properties of metal carbides which differ on the one hand from the corresponding pure metals and on the other hand from the insulating metal oxides.

For an estimate of the 'free' positron lifetime in the metal carbides according to equation (1) the two carbon valence electrons may be taken into consideration in addition to the four or five valence electrons per group IV or group V transition metal atom [12] in order to calculate the valence electron density. This, however, yields positron lifetimes lower than in the pure metals which is in contradiction with the present experimental findings.

Moreover, no simple relationship, as derived for metal oxides [7], was found for the differences  $\Delta\lambda^*$  in the annihilation rates and the differences

$$\Delta\eta^{\text{tot}} = \eta_{\text{MC}_y}^{\text{tot}} - \eta_{\text{M}}^{\text{tot}}$$

in the total electron densities between the metal carbides and the corresponding metals as expected from equation (2). For example, practically no difference in  $\Delta\lambda^*$

was found for niobium and tantalum carbides whereas the total electron density  $\eta^{\text{tot}}$  for  $\text{TaC}_y$  is three times higher than that of  $\text{NbC}_y$ .

A nearly linear relationship

$$\lambda^* = 17.9\eta^{\text{valM}} \quad (3)$$

is observed if we correlate the experimentally observed annihilation rates  $\lambda^*$  to the density of the metal valence electrons  $\eta^{\text{valM}}$  (see figure 1) neglecting the carbon valence electrons. Here  $\eta^{\text{valM}}$  is calculated by using four or five valence electrons for the group IV or group V metals, respectively, and an atomic volume as derived from the lattice parameter of the carbide. The description by equation (3) is rather similar to that in equation (1).

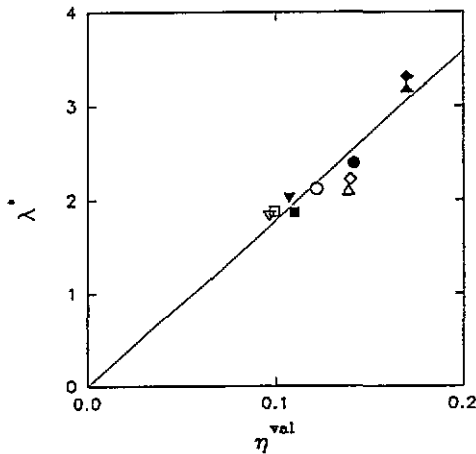


Figure 1. Variation of the normalized positron annihilation rate  $\lambda^*$  with the normalized density  $\eta^{\text{valM}}$  of metal valence electrons in the nearly stoichiometric carbides  $\text{TiC}_y$  (o),  $\text{ZrC}_y$  (▽),  $\text{HfC}_y$  (□),  $\text{NbC}_y$  (Δ), and  $\text{TaC}_y$  (◇) as well as in the pure metals (closed symbols). The solid line represents equation (3). Experimental errors of  $\lambda$  and  $\eta$  are less than the symbol size.

The direct correlation of the positron annihilation rate with the density of metal valence electrons indicates that positrons in non-stoichiometric metal carbides are annihilated mainly with metal valence electrons and that carbon electrons contribute to the annihilation to a minor extent.

This is supported by the variation of the positron lifetime in  $\text{NbC}_y$  with carbon content. Decreasing carbon content  $y$  (see figure 2) gives rise to an increase of the valence electron density  $\eta^{\text{valM}}$  of the metal sublattice due to a decrease of the atomic volume  $V_M$  [13] but to a decrease in the total valence electron density if the carbon valence electrons are taken into account.

The decrease of the positron lifetime, which occurs upon lowering the carbon content (see figure 2), is due to an increase of the electron density at the positron annihilation site and therefore points to predominant positron annihilation with the metal valence electrons. It should be mentioned that an extrapolation of the data in figure 2 to lower positron lifetime values nicely fits the positron lifetime data of pure Nb [3].

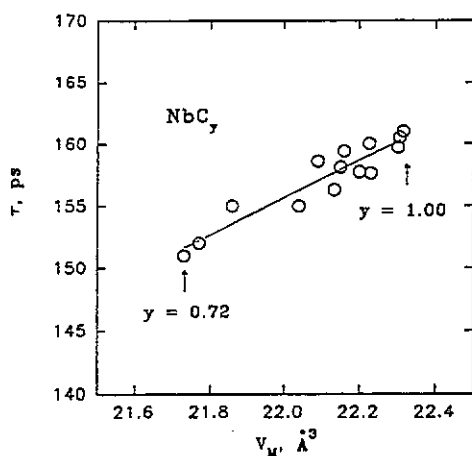


Figure 2. Variation of the positron lifetime  $\tau$  in  $\text{NbC}_y$  with the volume  $V_M$  of the metal atoms due to changes in the carbon contents  $0.72 < y < 1.00$  within the homogeneity region of the B1 structure. Experimental errors in  $\tau$  are  $\pm 1$  ps.

We may now ask the question why the positrons appear to be annihilated predominantly by metal valence electrons. One explanation could be the presence of vacant sites on the carbon sublattice in the range of atomic concentrations up to 0.3% even in nominally stoichiometric specimens which is strongly increased with deviation from stoichiometric composition. On a vacant carbon site the positron is surrounded by nearest-neighbour metal atoms exclusively and the positron lifetime is dominated by the valence electron density on the metal ion sublattice.

This is a situation similar to the positron state on interstitial sites in the undisturbed lattice of the pure metal. In fact, the free-positron lifetimes or annihilation rates  $\lambda^*$  of the pure metals fit into the scheme of figure 1 according to the corresponding valence electron densities. The positron lifetime in vacant lattice sites in pure Nb or Ta [3] are substantially higher than  $\tau_f$  and positron lifetimes in vacant sites of the metal sublattice in the carbides are also expected to be higher than the free lifetimes  $\tau_f$  there.

It should be mentioned that the positron wavefunction is unlikely to be localized in the carbon vacancies of the carbides because of the pretty high vacancy concentrations even in the nominally stoichiometric compounds.

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