Positron annihilation and Seebeck effect studies on silver-doped and oxygen-deficient tungsten trioxide

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Abstract. Studies of the positron annihilation and the Seebeck effect were performed on silver-doped tungsten trioxide of composition $Ag_{0.01}WO_3$, on the substoichiometric tungsten trioxide phase $WO_{2.975}$ and on $WO_{2.90}$ ($W_{20}O_{58}$). Both methods point out that there are some clusters of Ag^+ ions in the first case and oxygen vacancies in the second case. The clusters have some internal substructure and the formation enthalpy of the vacancy (or a positron trap) in this substructure was obtained as equal to 0.39 ± 0.01 eV. The measurements of the Seebeck effect showed that $Ag_{0.01}WO_3$ and $WO_{2.975}$ are normal n-type semiconductors whereas $WO_{2.90}$ exhibits metal-like properties.

1. Introduction

The silver-doped tungsten trioxide of composition $Ag_{0.01}WO_3$ was first obtained and investigated by Sienko and Mazumder [1]. The single crystals exhibited a strictly linear reversible and reproducible resistivity versus temperature dependence over the 300–900 K range; below 250 K the resistivity rose rapidly [2]. It was claimed that the Ag atoms were randomly distributed among the lattice holes of the ReO_3-type oxide framework (figure 1), being all ionized already at room temperature. The conduction electrons should occupy the W $5d(t_{2g})$–O $2p(\pi)$ orbital states of the empty antibonding band. Thus the Morin–Goodenough–Sienko model (see, e.g., [2, 3]) of the metallic-type tungsten oxide bronze (M_xWO_3) was applied to $Ag_{0.01}WO_3$. However, how this picture could agree with such a low conduction electron concentration (1.8×10^{20} cm^{-3}) and such a low carrier mobility (0.44 cm^2 V^{-1} s^{-1} at 300 K) as had to be accepted in this case still remains unclear.

The crystalline structure of $Ag_{0.01}WO_3$ as determined by Sienko and Mazumder is very close to that of the orthorhombic modification of WO_3 normally stable above 330 °C ($a = 0.735$ nm, $b = 0.373$ nm and $c = 0.385$ nm). However, it was found later [4] that a phase transition occurs in $Ag_{0.01}WO_3$ at 300 °C and that below that temperature the lattice keeps the characteristic distortions of monoclinic modification of WO_3 ($a = 0.735$ nm, $b = 0.746$ nm, $c = 0.385$ nm and $\beta = 90°55'$) stable between 17 and 330 °C. Nevertheless, even in this case the agreement between the observed and calculated d-spacings was not quite satisfactory and it was concluded that, with a distribution of Ag atoms far from random, the real structure of the $Ag_{0.01}WO_3$ must be more complicated.
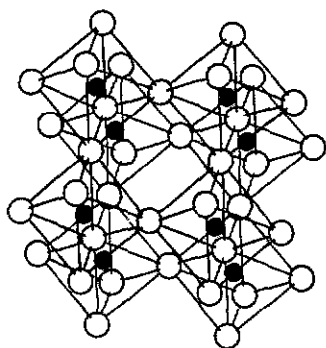
Figure 1. The ReO_x-type oxide framework. The lattice hole where the doped ion is located is surrounded by eight octahedra.

Additional support for this conclusion comes from self-diffusion studies made using [110]Ag on sintered $Ag_{0.01}WO_3$ pellets, which indicates that up to 830 °C the tendency to form some kind of Ag clusters is visible [5].

The above considerations suggest that it is reasonable not to pay too much attention to the formal analogy between $Ag_{0.01}WO_3$ and the substoichiometric tungsten bronzes but rather to search for analogies with the tungsten trioxide phases, WO_{3-x}, where $x \ll 1$. Many substances belonging to this group were obtained and investigated and their electrical behaviour as a function of the oxygen deficiency x and the temperature was found in general to be very complicated [6]. It is clear, however, that the missing oxygen atoms may act as electron donors in much the same sense as do the metal atoms inserted into the WO_3 host lattice. Moreover, it was found that there exists a tendency to eliminate the single oxygen vacancies from the WO_3 lattice in such a way that linear or planar aggregations of edge-sharing WO_6 octahedra are formed (figure 2). It may be expected that aggregation or clustering plays an important role both for the WO_{3-x} and for the metal-doped WO_3. In the present work we try to find some data to confirm this view.

2. Preparation and experimental details

$Ag_{0.01}WO_3$ was prepared from WO_3 and silver powder in appropriate proportions by thermal reaction in vacuum [5]. A fine polycrystalline shiny black product was obtained and x-ray powder diffractograms revealed full agreement with earlier data [4, 5]. It must be noted that samples with x appreciably different from 0.01 cannot be obtained by the thermal technique and probably also by any other method [1]. If larger amounts of silver were used for the syntheses, the excess of metal could easily be removed with hot HNO_3. In the opposite case the product was inhomogeneous, the WO_3 crystallites being easily recognizable with a polarization microscope. This shows that the homogeneity range of Ag-doped WO_3 is very narrow.

Preparations of $WO_{2.90}$ and $WO_{2.975}$ were obtained by thermal reduction of WO_3 with metallic tungsten powder [4]. The $WO_{2.90}$ (called β-WO_3) is dark blue in colour, its composition corresponds to the chemical formula $W_{20}O_{58}$ and $WO_{2.975}$ (called α-WO_3) is grey.

For the positron annihilation experiment we used an apparatus to measure the peak height of angular correlation of annihilation radiation (ACAR) as a function of temperature [7]. In this experimental set-up a [22]Na source (1 mCi) emitted positrons into a sintered sample and annihilation radiation was detected by two detectors placed
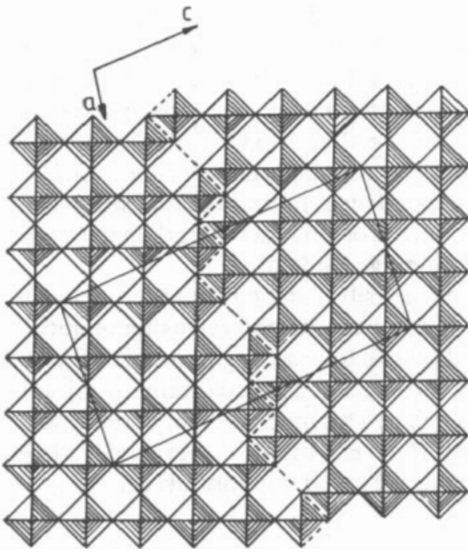
Figure 2. The quasi-two-dimensional structure (− − −) consists of shearing planes in the case of WO$_{2.90}$ (β-WO$_3$).
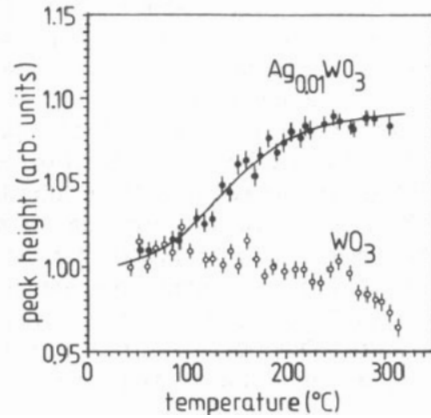
Figure 3. The peak height versus temperature for WO$_3$ and Ag$_{0.01}$WO$_3$: ————, best fit of the two-state model to the experimental data on Ag$_{0.01}$WO$_3$.

around the sample directly opposite each other. The geometric angular resolution was 3.3 mrad in the y direction and 378.8 mrad in the x-direction. The sample holder could be heated to a temperature of 320 °C. The source, the sample and the furnace were placed in a vacuum chamber evacuated to a pressure $p \leqslant 10^{-4}$ mbar.

Thermoelectric power measurements were made on sintered samples. The differential method was used with a temperature gradient of 1–3 K across the sample created by a heater and measured by means of copper–constantan thermocouple. The copper wires were used as the voltage leads.

3. Results and discussion

Studying the perovskite structure using the positron annihilation method is a difficult task because of the presence of many kinds of defect and trap which can affect the positron wavefunction. Hence the only measurements of positron lifetime which are sensitive to sample local electron densities and ACAR which can show that the fine details of the electronic structure applied to these materials are not easy to interpret. Such a complicated situation takes place in the case of high temperature superconductors where the positron annihilation method seems to fail. However, sometimes one can be successful when measuring the behaviour of the positron lifetime, Doppler broadening or ACAR, e.g. as functions of temperature. The character of these dependences can give some information about the processes which take place in the material studied. This technique was applied in our investigations. The apparatus described above is useful for studying the behaviour of vacancies and their clusters in thermal cycles especially in metals or alloys. We applied our apparatus to the investigation of four compounds: WO$_3$, WO$_{2.975}$, WO$_{2.90}$ and Ag$_{0.01}$WO$_3$. Each was powdered, shaped using a press

(10 MPa) into a pellet 2 mm thick and 10 mm in diameter and then sintered at 650 °C for 750 h. The reference measurement was performed on tungsten trioxide WO_3 (olive colour) which is an isolator. In figure 3, one can see that the peak height is constant with increasing temperature up to 150 °C; slightly above this temperature it starts to decrease, the decrease being rapid above 250 °C. One can see that at 330 °C the monoclinic structure of WO_3 changes into the orthorhombic structure and, in particular, the W^{+6} ion moves a little in the WO_6 octahedra. Such dependences indicate that positrons are sensitive to the configuration of O^{2-} and W^{6+} ions in the octahedra rather than the traps, which should not be generated in the temperature range studied.

Quite different behaviour is observed in the silver-doped tungsten trioxide $Ag_{0.01}WO_3$. The increase and then saturation in the peak height versus temperature (figure 3) is characteristic of, for example, metals with a low melting point (Cd, In, Pb, etc) where positrons are trapped by the thermal vacancies generated thermally [8]. It is interesting that the dependence obtained is reversible. This indicates that in the case of $Ag_{0.01}WO_3$ a thermal positron trap is generated. If we use the two-state model which describes the behaviour of positrons in poor metals very well, the formula for the peak height versus temperature is as follows:

$$N(T) = \frac{N_f(1 + \alpha T) + N_t \mu_t \exp(S_t/k_B) \exp(-H_t/k_B T)/\lambda_f}{1 + \mu_t \exp(S_t/k_B) \exp(-H_t/k_B T)/\lambda_f} \qquad (1)$$

where λ_f is the free annihilation rate, N_f and N_t correspond to the annihilation from the free state and the trapped state, μ_t is the positron trapping probability, k_B is the Boltzmann constant, and S_t and H_t are the entropy and enthalpy formation of the trap. We assume a linear effect of the thermal expansion of the lattice on N_f, described by the parameter α.

The plot of the best fit of equation (1) to the experimental data on $Ag_{0.01}WO_3$ is presented in figure 3. The value of the formation enthalpy H_t of the trap from our data is equal to 0.39 ± 0.01 eV. Assuming that $\lambda_f \simeq 1/300$ ps (according to Noguchi *et al* [9]), one can calculate that $\mu_t \exp(S_t/k_B) \simeq 1.6 \times 10^{14}$ s^{-1}. The same behaviour of the peak height and the same value of H_t and $\mu_t \exp(S_t/k_B)$ were obtained for $WO_{2.975}$ and $WO_{2.90}$ (figures 4 and 5). This indicates the common origin of positron trapping in the materials studied.

The results obtained are really peculiar. The enthalpy formation of a single vacancy, e.g. in Cd, is equal to 0.39 ± 0.04 eV and $\mu_v \exp(S_v/k_B) = 1.9 \times 10^{14}$ s^{-1} but the concentration of conductivity electrons equals 9.27×10^{22} cm^{-3} and it is three orders greater than in the case of $Ag_{0.01}WO_3$. The low value of the formation enthalpy of the trap is unexpected because the framework is based on covalent bonding. The explanation of these results seems to be that the interacting Ag^+ ions in the case of $Ag_{0.01}WO_3$ and oxide vacancies in the case of $WO_{2.975}$ and $WO_{2.90}$ create some clusters having an ordered substructure which strongly affects the positrons. The trap is just a negatively charged 'vacancy' in the substructure. Certainly the electron density in such clusters must locally be much higher than the average value mentioned above. Hence one can expect a strong interaction between the thermally generated vacancy and a positron. At temperatures above 200 °C the substructure becomes completely disordered because of the saturation of the peak height (figures 3–5). Let us compare the positron annihilation data with measurements of the thermoelectric power.

The Seebeck coefficient S is negative for all three substances in the whole temperature range 80–500 K investigated, but its magnitude and temperature dependence reveal a
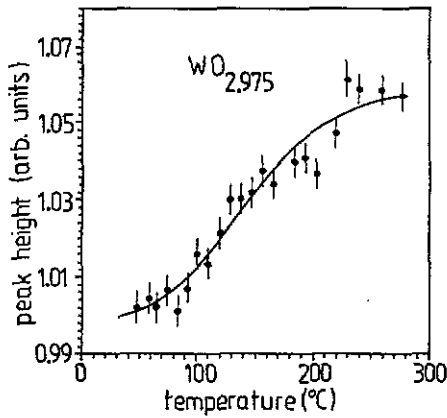
Figure 4. The peak height versus temperature for WO$_{2.975}$: ———, best fit of the two-state model to the experimental data.
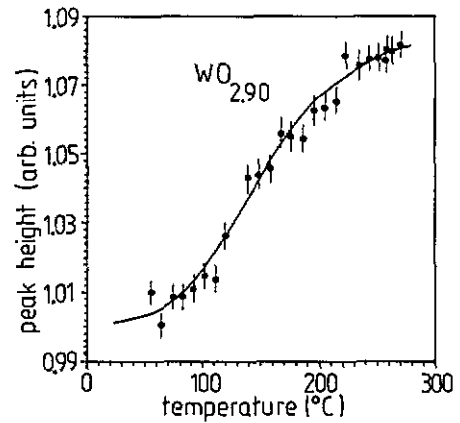
Figure 5. The peak height versus temperature for WO$_{2.90}$: ———, best fit of the two-state model to the experimental data.
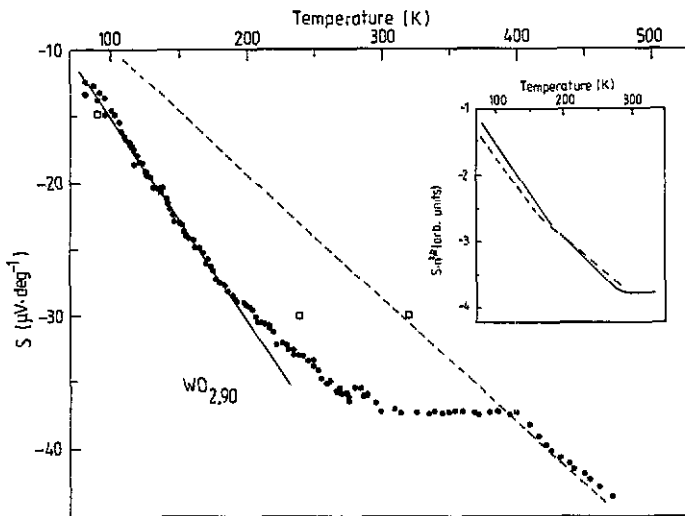

Figure 6. The Seebeck coefficient for WO$_{2.90}$ versus temperature: ———, quasi-free-electron model for a hypothetical bronze M$_x$WO$_3$ with $m_c^*/m_c = 3.5$, $x = 0.1$ and $p = 1$: – – –, the same model but with $p = 2$; □, experimental values obtained by Berak and Sienko [6]). The inset presents the Seebeck coefficient versus temperature curves normalized by the factor $n_c^{2/3}$ in arbitrary unit: ———, WO$_{2.90}$ (this work); – – –, Na$_{0.489}$WO$_3$ (from [12]).

significant difference between WO$_{2.90}$ (figure 6) and WO$_{2.975}$ and Ag$_{0.01}$WO$_3$ (figure 7). The absolute values of S for WO$_{2.90}$ are, for the same temperatures, more than one order of magnitude lower than those for the two other substances. Moreover, in the two cases, as one can see from figures 6 and 7, for temperatures below about 300 K the changes in S with increasing T have in the two cases opposite signs. The general conclusion is that WO$_{2.975}$ and silver-doped WO$_3$ are normal n-type semiconductors, whereas WO$_{2.90}$ behaves like a 'poor' metal.
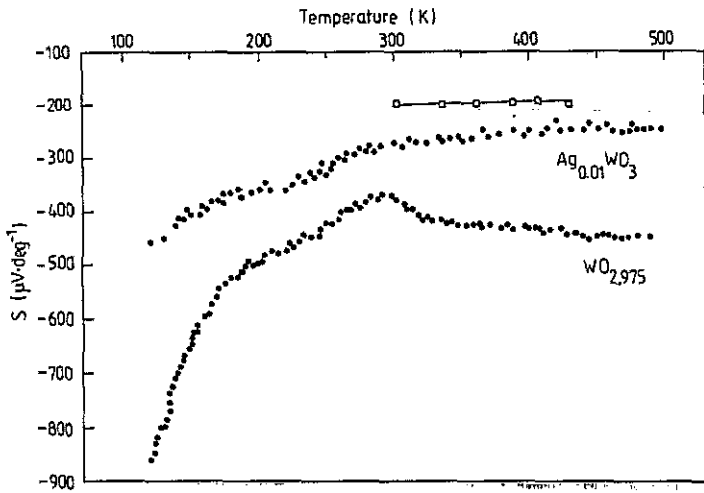
Figure 7. The Seebeck coefficient for $Ag_{0.01}WO_3$ and $WO_{2.975}$ versus temperature: □, experimental data obtained by Berak and Sienko [6] for $WO_{2.995}$.

The metallic character of $WO_{2.90}$ is certainly a fact of considerable interest. The possibly simplest but reasonable way to explain it is to draw an analogy between this compound and a tungsten bronze M_xWO_3 with equivalent electron concentration, e.g. $Na_{0.2}WO_3$ or $Na_{0.1}WO_3$ depending on whether we assume two or one free electrons coming from one oxygen atom removed from the WO_3. In normal conditions, in a lattice with the distorted perovskite-type structure (figure 1), the metallic conductivity of the bronze would collapse at $x = 0.22$ [10]. The fact that this limitation is not valid for $WO_{2.90}$ would be explained by its complex quasi-two-dimensional structure (figure 2) which consists of infinite (in two directions) blocks of almost undistorted WO_3 lattices separated from one another by parallel and equidistanced shearing planes, where the WO_6 octahedra are partially joined together by edges (figure 2). However, the character of the conducting band states would be the same as in the bronze, i.e. $W d(t_{2g})$–$O p(\pi)$. The measured thermoelectric power S is normally treated as a sum of the diffusion term S_d and lattice term S_g, and it is known that in the bronzes S_d, unlike S_g, is hardly sensitive to structural details [11]. It was shown for the metallic tungsten bronzes that S_d is the dominating term in wide ranges of temperatures and, moreover, that the free-electron model can give quite reasonable results [12]. We made an attempt to verify the validity of the above considerations by applying the free-electron model also to $WO_{2.90}$. If n_e denotes the concentration of the quasi-free electrons, then we have

$$S_d = \tfrac{2}{3}(\pi/3)^{2/3}(m_e k_B^2 T/e\hbar^2)(m_e^*/m_e)n_e^{-2/3} \tag{2}$$

where $\hbar$ is the Planck constant divided by 2π, m_e is the electron rest mass and m_e^* is the effective electron mass. As one can see in figure 6, the experimental $S(T)$ plot is in fact linear over the range 80–180 K and the full line represents the best fit to the measured points. However, equation (2) contains two independent parameters which should be determined: n_e and m_e^*/m_e. It can be seen that n_e could be determined from the stoichiometric and crystallographic data. However, in view of the peculiar laminar-type structure we used the simple formula

$$n_e = x_0 p a_0^{-3} \tag{3}$$

where x_0 denotes the number of deficient oxygen atoms per one W atom, p is the

number of electrons donated from one missing oxygen atom and a_0 (nm) = $(0.3785 + 0.008 \times p)$, which is twice the distance W–O in an undistorted WO_6 octa-hedron (figure 2) [10]. This gives $1.82 \times 10^{20}\,\text{cm}^{-3}$ and $3.64 \times 10^{20}\,\text{cm}^{-3}$ for $p = 1$ and $p = 2$, respectively.

Taking $p = 1$ we calculate from the slope of the full line that $m_e^*/m_e = 3.5$. From the standpoint of the postulated analogy with the tungsten bronze the above result is quite satisfactory. In fact, values of 3.48–3.72 were obtained from thermoelectric power studies on Na_xWO_3 [12]. It follows that by rescaling the dependence $S(T)$ for $WO_{2.90}$ and for a bronze with the factor $n_e^{2/3}$ we should obtain similar plots. Figure 6 illustrates this comparison for $Na_{0.489}WO_3$ using the data from [12].

The three points denoted by open squares in figure 6 represent the experimental values obtained by Berak and Sienko [6] for a single-crystal probe of $WO_{2.90}$. They do not diverge much from our sintered sample data. It is seen from figure 6 that for higher temperatures the experimental $S(T)$ plot deviates more and more from a linear $S_d(T)$-dependence; between 300 and 400 K a plateau is observed. The dependence of the Seebeck coefficient upon the temperature for $T \geqslant 180$ K is no doubt influenced by the increasing importance of the lattice term $S_g(T)$. Assuming that $S_d(T)$ can be extrapolated to higher temperatures we can write

$$S_g(T) = S(T) - S_d(T) = S_n(T) + S_u(T) \tag{4}$$

where S_n and S_u refer to normal and umklapp electron–phonon interactions, respectively. It was shown that the normal processes should give a negative and the umklapp processes a positive contribution to S_g [13]. A simple model based on this assumption was shown to be in general agreement with the experimental results for cubic Na_xWO_3 [11]. For $WO_{2.90}$ we can see that S_g is positive and increases with increasing T in the whole 180–400 K range. However, owing to the sensitivity of the phonon-drag processes to details of the lattice structure no quantitative conclusions can be formulated, because in the case of $WO_{2.90}$ they would be rather complicated compared with Na_xWO_3.

At 400 K an abrupt fall in the $S(T)$ experimental curve is observed in figure 6. The part of the plot between 400 and 500 K is linear and it coincides almost exactly with the extrapolated (broken) line which represents $S_d(T)$ calculated for the same effective mass ($m_e^*/m_e = 3.5$) but assuming two mobile electrons ($p = 2$) per one deficient oxygen atom. This undoubtedly is significant, but at this time we have no further evidence supporting this hypothesis.

The thermoelectric power of $WO_{2.975}$ and $Ag_{0.01}WO_3$, as presented by the $S(T)$-curves in figure 7, indicates in general the same mechanism; it confirms the assumption that, if there is a sufficiently low concentration, donor atoms act in the same manner as deficient oxygen atoms. For comparison we show also the values of Berak and Sienko [6] for a sample with composition $WO_{2.995}$ (open squares). It is evident that $Ag_{0.01}WO_3$ behaves as a typical n-type semiconductor and has, at least in view of its thermoelectric properties, nothing in common with the metallic tungsten bronzes. Unfortunately we were unable to perform on our sintered samples reliable measurements of the electrical resistivity of $Ag_{0.01}WO_3$. Hence a comparison with the results of Sienko and Mazumder [1] is not possible.

4. Conclusion

A general impression resulting from the positron annihilation experiment is that both silver-doped WO_3 and the oxygen-deficient oxides $WO_{2.975}$ and $WO_{2.90}$ behave in a

manner characteristic of metals with low melting temperatures. This can be explained assuming that the inserted doped ions or missing oxygen atoms aggregate, forming clusters with a high local concentration of virtually mobile electrons and an ordered substructure in which a positron trap can be thermally generated. There is still the open question about the structure of the trap and how it is generated with temperature. The above picture also agrees with the observed semiconducting properties of $Ag_{0.01}WO_3$ and $WO_{2.975}$ as revealed by the Seebeck effect measurements. The low concentration of the clusters in these compounds cannot create any continuous regions across the crystals for moving electrons. The opposite holds for $WO_{2.90}$ ($W_{20}O_{58}$) where its metallic properties can be explained as a result of the relatively high concentration of virtual mobile electrons which can move through the ordered lattice formed by parallel WO_3 layers with inserted shearing planes.

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