

# Study of grain boundaries in polycrystalline Cr, Ta and W using nuclear gamma-resonance spectroscopy: Formation enthalpies of vacancy-oxygen complexes and single vacancies in grain boundaries, and dynamic properties of the grain boundary core in polycrystals of BCC metals

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The formation of complexes of vacancies with oxygen atoms (complexes-VacO) in the core of grain-boundary (GB) leads to a dependency of the isomer shifts  $\delta_1$  of components-1 in NGR emission spectra of  $^{57}\text{Co}$ ( $^{57}\text{Fe}$ ) atomic probes localized in the GB core on the annealing temperature of polycrystalline metals in a technical vacuum. The formation enthalpies of complexes-VacO,  $Q_{\text{cpl},1}$ , and single vacancies,  $Q_{\text{vac},1}$ , in the GB core (states-1) in Cr, Ta and W polycrystals have been measured for the first time. Dynamic contributions to formation enthalpies  $Q_{\text{vac},1}$  of single vacancies localized in the GB core in the state-1 and dynamic contributions to formation enthalpies  $Q_{\text{cpl},i}$  of complexes-VacO, which were localized in the lattice regions adjacent to GB's (Adjacent Lattice Regions, ALR's), states-2, and in the GB core, states-1, have been separated. The dynamic contribution to the formation enthalpy  $Q_{\text{vac},1}$  of vacancies and  $Q_{\text{cpl},1}$  of complexes-VacO in the GB core was several times smaller than the contribution to the formation enthalpy  $Q_{\text{vac},\text{vol}}$  of vacancies in the bulk of the crystallites because of low-frequency resonance modes of local collective vibrations of intrinsic atoms in the GB core. © 2005 Springer Science + Business Media, Inc.

## 1. Introduction

Internal interfaces, including grain boundaries (GB's) in polycrystals, determine basic physical properties of nanostructures [1]. GB's have been studied systematically, in particular, by the method [2–6], in which are used: (a) atomic probes (AP's) providing spectral information about the structure and properties of states occupied by these AP's and (b) grain-boundary diffusion of AP's ensuring their localization in the GB core and in adjacent lattice regions (ALR's). The NGR spectroscopy was used [2–7] as a tool for determination of the structure and properties of states occupied by  $^{57}\text{Co}$ ( $^{57}\text{Fe}$ ) AP's during grain-boundary diffusion in polycrystals [2].

NGR emission spectra of  $^{57}\text{Co}$ ( $^{57}\text{Fe}$ ) AP's, which are introduced by GB diffusion, contain only two components (Fig. 1): the component-1 and the component-2

caused by  $^{57}\text{Co}$ ( $^{57}\text{Fe}$ ) AP's localized in the GB core (states-1) and ALR's (states-2) [3–7] respectively. The isomer shifts  $\delta_1$  and  $\delta_2$  of components-1 and -2 depend on the annealing temperature of polycrystals in a vacuum.

For example, after the annealing at the first lowest-temperature the isomer shifts  $\delta_2$  of components-2 in NGR emission spectra of  $^{57}\text{Co}$ ( $^{57}\text{Fe}$ ) AP's become much smaller than the isomer shifts  $\delta_{\text{vol}}$ , which characterize volumes of pure metals (Fig. 2) [3–6]. The difference  $\delta_2 - \delta_{\text{vol}} < 0$  is due to doping of the polycrystals with oxygen during annealing in a technical oil-free vacuum of about  $10^{-6}$ – $10^{-5}$  Torr. The macroscopic volume of the oxygen-doped metal increases because the oxygen impurity has a positive relaxation volume  $v_0 > 0$  in metals [8, 9]. The growth of the macroscopic volume of the metals leads to the decrease in

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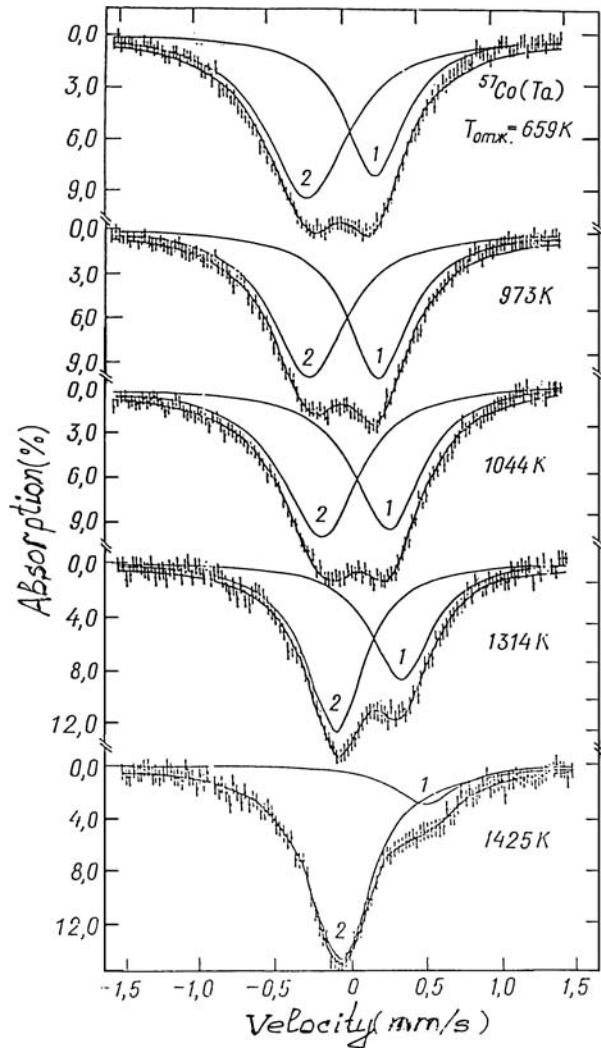


Figure 1 NGR emission spectra of  $^{57}\text{Co}(^{57}\text{Fe})$  atomic probes measured at room temperature after annealing of polycrystalline Ta at temperatures shown in the figure.

the density of conduction  $s$ -electrons in the bulk and in the GB core. In this case, the density of  $s$ -electrons in the AP's core decreases (Fig. 2) and the isomer shifts  $\delta$  of the corresponding components in NGR emission spectra of  $^{57}\text{Co}(^{57}\text{Fe})$  diminish [8, 10].

Vacancies in the bulk [11–14] and in the GB core [15, 16] in metals have a negative relaxation volume  $v_{\text{vac}} < 0$ . The growth (or increase) in the vacancy concentration with increasing annealing temperature is followed by the decrease in the interatomic spacing. Both the density of valence  $s$ -electrons in the GB core and the isomer shifts  $\delta_1$  and  $\delta_2$  (Figs 2 and 3) of the components-1 and -2 in NGR emission spectra of  $^{57}\text{Co}(^{57}\text{Fe})$  [17–19] increase correspondingly.

Fig. 3 presents temperature dependences of the isomer shifts  $\delta_1$  of the NGR spectrum component-1, which are due to the emission of AP's localized in the GB core in Cr, Ta and W polycrystals. The dependencies  $\delta(1/T)$  in Figs 2 and 3 are similar. This suggests nearness of the states of point defects localized in ALR's and the GB core in the metals [17–19]. Specific features of the dependencies  $\delta_1(1/T)$  (the absence of plateaus, nearly equal slopes of the linear sections in the  $\delta_i(1/T)$  dependencies for each metal), which were measured for

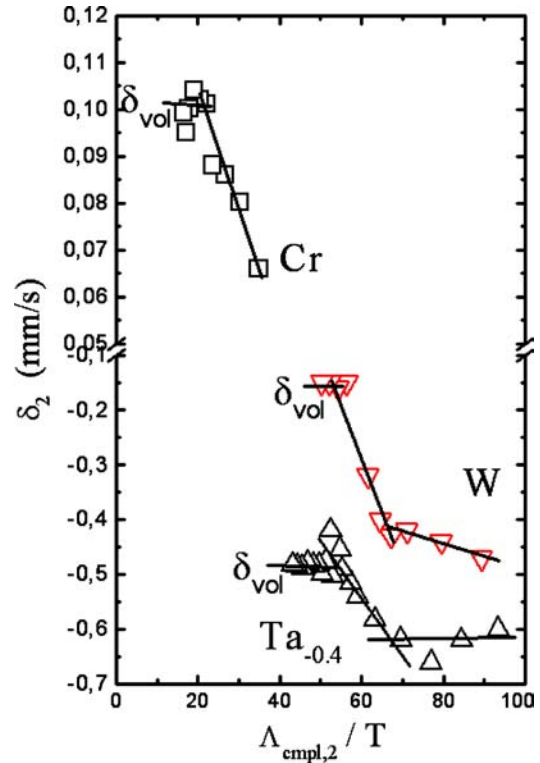


Figure 2 Dependencies  $\delta_2(1/T)$  of the isomer shifts of components-2 in NGR emission spectra of  $^{57}\text{Co}(^{57}\text{Fe})$ , which were localized in ALR's in Cr, Ta and W polycrystals. The segments are only guides for the eyes. The index number for Ta is the  $\delta_2(\text{Ta})$  shift value.

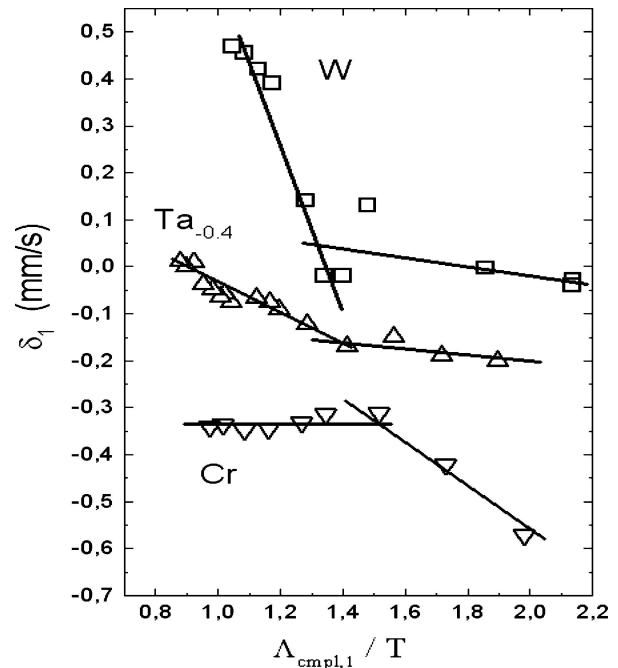


Figure 3 Dependencies  $\delta_1(1/T)$  of the isomer shifts of components-1 in NGR emission spectra of  $^{57}\text{Co}(^{57}\text{Fe})$ , which were localized in GB cores in Cr, Ta and W polycrystals. The segments are only the guide for the eyes.

Ta and W polycrystals, are determined by the composition of complexes-VacO, which is limited by the atomic structure of the GB core [19].

In this study, Arrhenius dependences of the contribution of  $\delta_{\text{cmpl},1}$  to the isomer shift  $\delta_1$  of the component-1 in the NGR emission spectrum of  $^{57}\text{Co}(^{57}\text{Fe})$  were

used to determine formation enthalpies  $Q_{\text{cpl},1}$  of complexes-VacO in the GB core in polycrystalline Cr, Ta and W. The measured enthalpies  $Q_{\text{cpl},1}$  exhibit a linear dependence on the corresponding “homologous temperatures”  $\Lambda_{\text{cpl},1}$ . Formation enthalpies  $Q_{\text{vac},1}$  of single vacancies in the GB core were determined using the linear dependence  $\{Q(\Lambda)\}_{\text{cpl},1}$  and the calculated [20] minimum formation enthalpy of vacancies in the GB core in Mo. Dynamic contributions to the formation enthalpies  $Q_{\text{vac},j}$  and  $Q_{\text{cpl},j}$  of vacancies and VacO complexes, which were localized in the GB core and ALR’s, were found as ratios of empirical parameters determining the “homologous temperatures”  $\Lambda_{i,j}$ . The dynamic contribution of local collective vibrations to the formation enthalpy  $Q_{\text{vac},1}$  of vacancies in the GB core was several times smaller than the contribution to the formation enthalpies  $Q_{\text{vac},\text{vol}}$  of vacancies in the bulk of polycrystals of transition Cr, Ta and W *d*-transition metals. Local lowfrequency resonance modes of vibrations of intrinsic atoms determine small dynamic contributions to the formation enthalpies  $Q_{i,1}$  of point defects in the GB core.

## 2. Theoretical background

The change of the isomer shift  $\delta$  of the NGR spectrum component with the concentration  $C$  of point defects in a metal is written as [21]:

$$d\delta/dC = (\partial\delta/\partial \ln V)_C(d \ln V/dC) + (\partial\delta/\partial C)_V. \quad (1)$$

Here the indices  $C$  and  $V$  denote the parameter to be fixed, namely, the defect concentration or the macroscopic volume respectively. The variation rates  $(\partial\delta/\partial \ln V)_C$  of the isomer shifts with the volume  $V$  were determined in studies of the effect of a high pressure  $P$  on the isomer shifts of the volume components in NGR emission spectra of  $^{57}\text{Co}$ ( $^{57}\text{Fe}$ ) AP’s [22]. These rates are constant for each metal:

$$(\partial\delta/\partial \ln V)_C = -\chi, \quad (2)$$

The coefficient  $d \ln V/dC$  in (1) denotes the sum of relaxation volumes  $v_i$  of point defects as determined from X-ray diffraction data [8, 9, 21]:

$$d \ln V/dC = \sum v_i. \quad (3)$$

The second term in the expression (1), which describes the direct effect of a point defect on the electronic structure of the nearest environment of AP’s, is calculated from “the first principles” for  $^{57}\text{Co}$ ( $^{57}\text{Fe}$ ) AP systems in iron doped with impurities [23]. The comparison of theoretically calculated isomer shifts [23] and the data of the NGR spectroscopic analysis of O(Ta), O(W) and O(Cr) [8, 17–19] solid solutions showed that only the first term in the expression (1) could be used with a good approximation.

From the relationships (1)–(3) it follows

$$\delta = -\chi \sum (vC)_i + (\delta_{\text{intr}})_{C=0}. \quad (4)$$

The isomer shift  $\delta_1$  of the component-1 in the NGR emission spectrum of AP’s localized in the GB core in the solid solution of point defects in a metal, which was annealed in a technical vacuum of about  $10^{-6}$ – $10^{-5}$  Torr, includes the following contributions:

$$\delta_1 = (\delta_{\text{intr}} - |\delta_{\text{O}}| + \delta_{\text{cpl}})_1, \quad (5)$$

where  $\delta_{\text{intr},1}$ ,  $\delta_{\text{O},1}$  and  $\delta_{\text{cpl},1}$  stand for partial contributions to the isomer shift  $\delta_1$  from AP’s localized in a pure GB core or GB cores containing only free oxygen impurities or only complexes-VacO respectively.

The temperature dependence of  $\delta_{\text{cpl},1}$  in (5) is determined by the concentration  $C_{\text{cpl},1}$  of complexes-VacO in the GB core if the concentration  $C_{\text{O}}$  of oxygen atoms is constant. The concentration of complexes-VacO, each comprising one oxygen atom and one vacancy, is given by the relationship [24]:

$$C_{\text{cpl},1} = \{C_{\text{O}}C_{\text{vac}} \exp(E_{\text{cpl},x})\}_1. \quad (6)$$

Here  $C_{\text{vac},1}$  denotes the concentration of vacancies in the GB core,  $E_{\text{cpl},1}$  is the enthalpy of interaction between partners in a complex-VacO, and  $x = 1/RT$  ( $R$  being the gas constant and  $T$  the annealing temperature). The vacancy concentration  $C_{\text{vac}}$  is given by the relationship [25]:

$$C_{\text{vac}} = (C_{\text{vac}})_0 \exp(-Q_{\text{vac}}x), \quad (7)$$

where  $(C_{\text{vac}})_0 = \exp(S/R)$  is a pre-exponential factor,  $S_{\text{vac}}$  and  $Q_{\text{vac}}$  denote the entropy and enthalpy of vacancy formation respectively. From (6) and (7) it follows for complexes-VacO:

$$C_{\text{cpl},1} = \{\text{const.} \exp[-(Q_{\text{vac}} - E_{\text{cpl}})x]\}_1. \quad (8)$$

The formation enthalpy  $Q_{\text{cpl},1}$  of complexes-VacO in the GB core is determined from the Arrhenius dependences of  $\delta_{\text{cpl},1}$  and the relationship (8):

$$\begin{aligned} Q_{\text{cpl},1} &= -\partial \ln \delta_{\text{cpl},1} / \partial x = -\partial \ln \delta_{\text{cpl},1} / \partial x \\ &= (Q_{\text{vac}} - E_{\text{cpl}})_1. \end{aligned} \quad (9)$$

## 3. Results and discussion

Measurements of the NGR emission spectrum of AP’s were made at room temperature for the polycrystalline samples (the source) and the resonance absorber after each annealing in the isochronal annealing series. For details of the sample preparation, annealing and measurement of NGR spectra refer to [3–7].

### 3.1. Enthalpies of formation of complexes-VacO in the GB Core in Cr, Ta and W polycrystals

Annealing temperatures,  $A_1 = (\delta_{\text{intr}} - |\delta_{\text{O}}|)_1$  values, which were used for calculating the contributions  $\delta_{\text{cpl},1}$  by the relationship (5), and contributions  $\delta_{\text{cpl},1}$  to the isomer shifts  $\delta_1$  are given in Table I. Similarly to

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TABLE I Annealing temperatures  $T_{(\kappa)}$ , values of  $A_1$  (mm/s), and contributions  $\delta_{\text{cpl},1}$  (mm/s) to the isomer shifts  $\delta_1$  of components-1 in NGR spectra of Cr, Ta and W polycrystals

Cr		Ta		W	
$A_1 = -0.83$		$A_1 = 0.198$		$A_1 = -0.04$	
$T$	$\delta_{\text{cpl},1}$	$T$	$\delta_{\text{cpl},1}$	$T$	$\delta_{\text{cpl},1}$
526	0.038	659	0.002	624	0.004
555	0.104	729	0.013	716	0.013
585	0.18	800	0.052	833	0.017
622	0.256	884	0.033	1000	0.04
671	0.347	973	0.079	1087	0.131
762	0.48	1044	0.111	1205	0.423
		1073	0.127	1290	0.469
		1114	0.136	1400	0.52
		1202	0.125		
		1224	0.143		
		1242	0.137		
		1275	0.152		
		1314	0.165		
		1353	0.211		
		1391	0.202		
		1425	0.213		

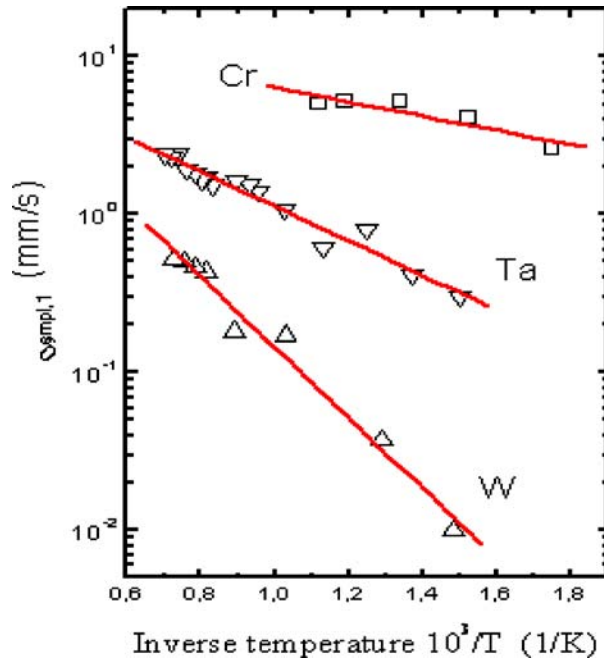


Figure 4 Arrhenius dependencies of the contributions  $\delta_{\text{cpl},1}$  to the isomer shifts  $\delta_1$  of components-1 in NGR emission spectra of  $^{57}\text{Co}(^{57}\text{Fe})$ , which were localized in GB cores in Cr, Ta and W polycrystals. The straight lines were drawn by the least squares method.

[18],  $(\delta_1)_{\text{min}}$  values, which were measured at temperatures of about  $0.2T_{\text{melt}}$  ( $T_{\text{melt}}$  being the matrix melting point), were taken as  $A_1$ . At these temperatures the vacancy concentration and, correspondingly, the concentration of complexes-VacO in the GB core is small and below the sensitivity limit of the measurement method and, therefore, one may use  $(\delta_1)_{\text{min}} = A_1$ .

The Arrhenius dependencies of  $\delta_{\text{cpl},1}$ , which are shown in Fig. 4, are well-approximated by straight lines when the concentrations change by 1 order or 2 orders of magnitude. Formation enthalpies  $Q_{\text{cpl},1}$  of complexes-VacO in GB cores in Cr, Ta and W are given in the line 4 of Table II.

TABLE II “Homologous temperatures”  $\Lambda_{i,j(\kappa)}$ ,  $Q_{\text{cpl},1}$  denotes formation enthalpies of VacO complexes in the GB core in Cr, Ta and W,  $(Q_{\text{Vac},1})_{\text{theor}}$  is the calculated minimum formation enthalpy of vacancies in the core of a special GB in Mo,  $(Q_{\text{cpl},1})_{\text{Mo}}$  is the estimated formation enthalpy of VacO complexes in the GB core in Mo,  $(E_{\text{cpl},1})_{\text{Mo}}$  is the estimated enthalpy of interactions between partners in VacO complexes,  $Q_{\text{Vac},1}$  is the formation enthalpy of vacancies in the GB core in Cr, Ta and W. All enthalpies are in kJ/mole

NN	Metals	Cr	Ta	W	Mo
1	Reference		Present study		[20]
2	Type of GB's		Large-angle GB's of common type in polycrystals		$\Sigma 3$ (112)[110]
3	$\Lambda_{\text{cpl},1}$	1134	1258	1443	1220
4	$Q_{\text{cpl},1}$	$10.5 \pm 2.6$	$21.3 \pm 2.9$	$43.8 \pm 2.4$	
5	$(Q_{\text{Vac},1})_{\text{theor}}$				58
6	$(Q_{\text{cpl},1})_{\text{Mo}}$				$19 \pm 2$
7	$(E_{\text{cpl},1})_{\text{Mo}}$				$39 \pm 2$
8	$Q_{\text{Vac},1}$	$49 \pm 4.6$	$60 \pm 5.0$	$83 \pm 4.4$	

3.2. The enthalpies  $Q_{\text{cpl},1}$  depend linearly on “homologous temperatures”  $\Lambda_{\text{cpl},1}$ . The measured enthalpies of formation of vacancies in the bulk of metals “ $Q_{\text{Vac},\text{vol}}$ ” are proportional to the sum of products

$$Q_{\text{Vac},\text{vol}} \propto (\alpha T_{\text{melt}} + \beta \theta_D)_{\text{Vac},\text{vol}} = \Lambda_{\text{Vac},\text{vol}} \quad (10)$$

of the empirical parameters  $(\alpha, \beta)_{\text{Vac},\text{vol}}$  and thermodynamic constants  $(T_{\text{melt}}, \theta_D)$  [26]. Here  $\theta_D$  is the Debye temperature of the matrix bulk [27], the quantity  $\Lambda_{i,j}$ , on which the enthalpies  $Q_{i,j}$  depend linearly [26], is called the “homologous temperature”, and the indices “ $i$ ” and “ $j$ ” stand for the type of point defects and the region of its localization respectively. The dependences  $\{Q(\Lambda)\}_{\text{Vac},\text{vol}}$  of the measured enthalpies  $Q_{\text{Vac},\text{vol}}$  [26] for vacancies formed in the bulk of FCC and BCC metals are shown in Fig. 5. Analogous linear dependencies

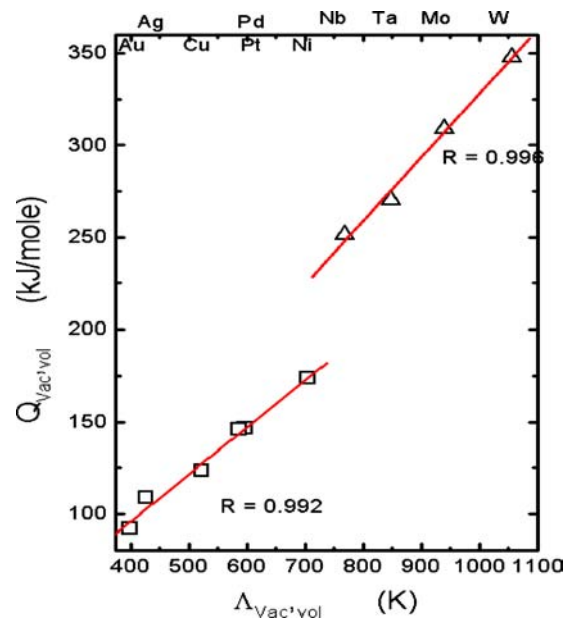


Figure 5 Dependencies  $\{Q(\Lambda)\}_{\text{Vac},\text{vol}}$  of the measured formation enthalpies  $Q_{\text{Vac},\text{vol}}$  of vacancies in the bulk of FCC and BCC metals [26]. The straight lines were drawn using the least squares method.

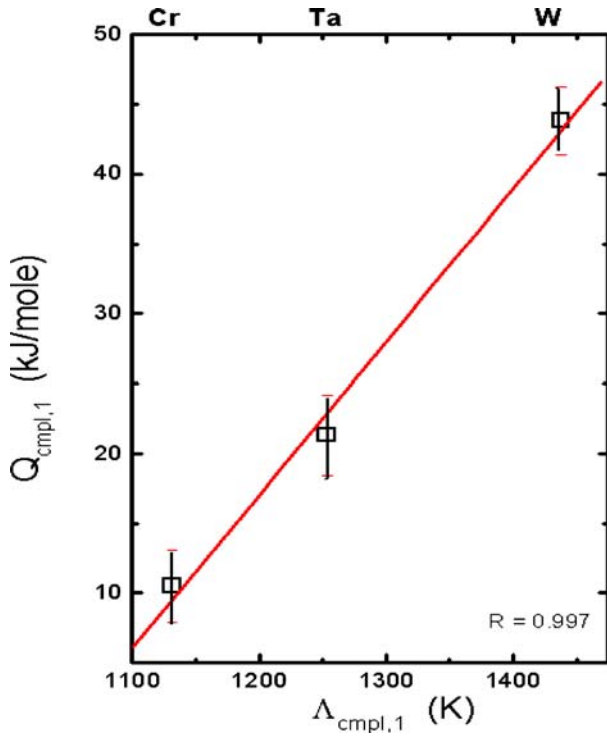


Figure 6 Dependence  $\{Q(\Lambda)\}_{\text{c mpl},1}$  of the measured formation enthalpies  $Q_{\text{c mpl},1}$  of VacO complexes in the GB core. The straight line was drawn by the least squares method.

$Q(\Lambda)_{i,j}$  will be used to determine dynamic contributions to formation enthalpies  $Q_{i,j}$  of point defects in different regions of polycrystals.

Measured dependencies  $\{Q(\Lambda)_{\text{c mpl},1}$  of formation enthalpies  $Q_{\text{c mpl},1}$  of complexes VacO in the GB core of Cr, Ta and W polycrystals (Fig. 6) are also approximated very accurately by a straight line (the correlation coefficient  $R = 0.997$ ), which is described by the equation:

$$Q_{\text{c mpl},1} = -(126.3 \pm 5.2) + (0.1224 \pm 0.0042)\Lambda_{\text{c mpl},1}. \quad (11)$$

### 3.3. Determination of formation enthalpies of vacancies in the GB core in Cr, Ta and W polycrystals

Formation enthalpies  $Q_{\text{Vac},1}$  of single vacancies in the GB core in Cr, Ta and W polycrystals are determined by the following procedure. The formation enthalpy  $(Q_{\text{c mpl},1})_{\text{Mo}}$  of hypothetical complexes-VacO in the GB core in Mo (line 6 in Table II) is found first. To this end, we use the equation for the straight line (11) the “temperature”  $\Lambda_{\text{c mpl},1} = 1220 \text{ K}$  from the relationship (10), and the parameters  $(\alpha, \beta)_{\text{c mpl},1}$  for BCC metals (see Section 3.4).

Secondly, we take the estimated enthalpy  $(E_{\text{c mpl},1})_{\text{Mo}}$  (line 7, Table II) of interaction, which appears the Equation (9). The enthalpy  $(E_{\text{c mpl},1})_{\text{Mo}}$  is defined as the difference

$$(E_{\text{c mpl},1})_{\text{Mo}} = (Q_{\text{c mpl},1})_{\text{Mo}} - (Q_{\text{Vac},1})_{\text{Mo}} \quad (12)$$

of the estimated enthalpy  $(Q_{\text{c mpl},1})_{\text{Mo}}$ , which was determined above, and the calculated [20] enthalpy

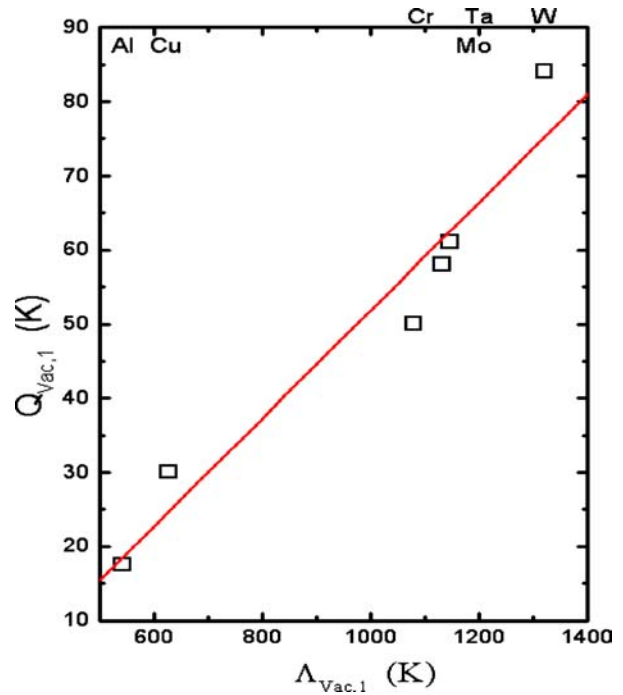


Figure 7 Dependence  $\{Q(\Lambda)\}_{\text{Vac},1}$  of the measured enthalpies  $Q_{\text{Vac},1}$  for Cr, Ta and W and theoretical [15, 20, 29] enthalpies  $(Q_{\text{Vac},1})_{\text{theor}}$  for Mo, Cu and Al. The straight line was drawn by the least squares method.

$(Q_{\text{Vac},1})_{\text{Mo}}$  of formation of a vacancy in a special large-angle GB core in Mo. The enthalpy of interaction between partners in hypothetical complexes-VacO in the GB core in Mo equals  $(E_{\text{c mpl},1})_{\text{Mo}} \cong 40 \text{ kJ/mole}$ . The energy of interaction between interstitial impurities (H, O) and vacancies is essentially the same for metals [28]. Therefore, let us assume  $(E_{\text{c mpl},1})_{\text{Mo}} = (E_{\text{c mpl},1})_{\text{BCC}}$  for BCC metals.

Finally, formation enthalpies  $Q_{\text{Vac},1}$  (line 8, Table II) of vacancies in the GB core in polycrystalline Cr, Ta and W are found from the relationship.

$$Q_{\text{Vac},1} = Q_{\text{c mpl},1} + (E_{\text{c mpl},1})_{\text{BCC}} \quad (13)$$

It is interesting to compare  $Q_{\text{Vac},1}$  values (line 8, Table II) with calculated minimum enthalpies  $(Q_{\text{Vac},1})_{\text{theor}}$  of formation of vacancies in a special large-angle GB core in Cu and Al [15, 29].

The common linear dependence of enthalpies  $Q_{\text{Vac},1}$  for BCC metals and  $(Q_{\text{Vac},1})_{\text{theor}}$  for FCC metals on temperatures  $\Lambda_{\text{Vac},1}$  is shown in Fig. 7. The correlation coefficient  $R = 0.981$  of this straight line, which was calculated by the least squares method, is just a little smaller than the analogous coefficients of the linear dependences given in Fig. 5. It should be noted that the dependence  $\{Q(\Lambda)\}_{\text{Vac},1}$  was constructed using results obtained for BCC and FCC metals. As can be seen from Fig. 5, dependencies  $\{\{Q(\Lambda)\}_{\text{Vac},\text{vol}}\}$  for these metals do not coincide. It may be assumed therefore that the same difference is responsible for a greater scatter of points around the linear dependence  $\{Q(\Lambda)\}_{\text{Vac},1}$ , which approximates  $Q_{\text{Vac},1}$  values for BCC and FCC metals.

To make the discussion of point defects in the GB core and ALR's more complete, let us use the linear dependence  $\{Q(\Lambda)\}_{\text{c mpl},2}$  (Fig. 8) of the enthalpies  $Q_{\text{c mpl},2}$ , which determine the concentration of

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TABLE III Empirical parameters  $(\alpha, \beta)_{i,j}$ , dynamic contributions  $\gamma_{i,j}$  to formation enthalpies  $Q_{i,j}$  of vacancies and VacO complexes in the crystallite volume, ALR's and the GB core in polycrystalline Cr, Ta and W

1	Defect localization region	Crystallite volume	ALR's	GB core	
				Vacancy	VacO complex
2	Type of defect	Vacancy	VacO complex	VacO complex	Vacancy
Empirical parameters					
3	$\alpha$	$0.170 \pm 0.035$ ;	$0.148 \pm 0.030$ ;	$0.3347 \pm 0.0087$ ;	$0.3090 \pm 0.0096$ ;
4	$\beta$	$0.830 \pm 0.035$	$0.852 \pm 0.030$	$0.6653 \pm 0.0089$ .	$0.6910 \pm 0.0096$ .
5	Dynamic contributions to the enthalpies $Q_{i,j}$ $\gamma_{i,j} = (\beta/\alpha)_{i,j}$	$4.88 \pm 1.12$	$5.76 \pm 1.35$	$1.988 \pm 0.080$	$2.25 \pm 0.10$

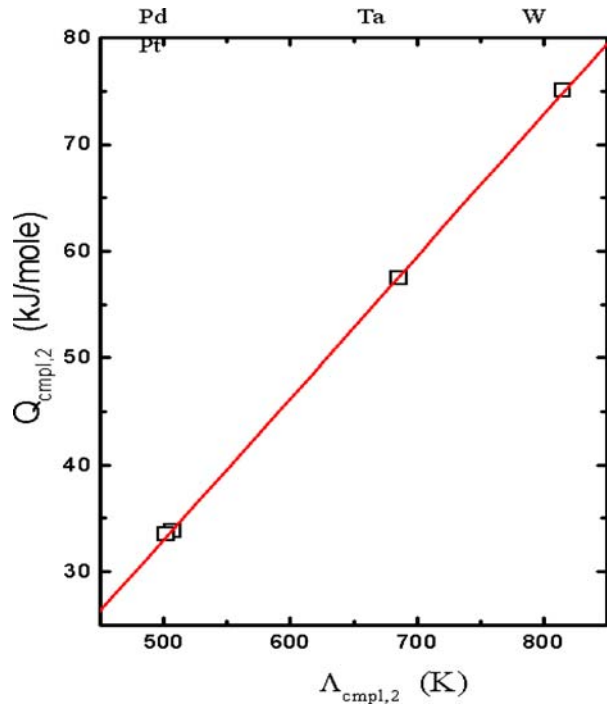


Figure 8 Dependence  $\{Q(\Lambda)\}_{\text{cpl},2}$  of the measured formation enthalpies  $Q_{\text{cpl},2}$  of VacO complexes in ALR's. The straight line was drawn by the least squares method.

complexes-VacO in ALR's in Pd, Pt, Ta and W [18]. The linear dependence  $\{Q(\Lambda)\}_{\text{cpl},2}$  is characterized by a large correlation coefficient  $R = 0.9993$ .

### 3.4. Dynamic contributions to formation enthalpies of vacancies and VacO complexes in the GB core and ALR's

Let us describe dynamic contributions to the formation enthalpies of  $i$ -th point defects in the  $j$ -th region of a polycrystal by the relation

$$\gamma_{i,j} = (\beta/\alpha)_{i,j}, \quad (15)$$

where  $\alpha$  and  $\beta$  denote the empirical parameters (Table III) from the relationship (10).

Nearly equal dynamic contributions (Table II)  $\gamma_{\text{vac},1}$  and  $\gamma_{\text{cpl},1}$  are much smaller than the value of the "internal standard"  $\gamma_{\text{vac},\text{vol}}$ , that is, the dynamic contribution to the formation enthalpies of vacancies in the volume. The ratio of the dynamic contributions to the formation

of point defects in the GB core and in the lattice is

$$\gamma_{i,1}/\gamma_{i,\text{latt}} \cong 0.4 \pm 0.1, \quad (16)$$

where  $\gamma_{i,1} = (\gamma_{\text{cpl},1} + \gamma_{\text{vac},1})/2$  and  $\gamma_{i,\text{latt}} = (\gamma_{\text{cpl},2} + \gamma_{\text{vac},\text{vol}})/2$ . The relationship (16) reflects the presence of low-frequency resonance modes in the local spectrum of collective vibrations (LSCV) of the GB core itself. This fact was confirmed by calculations [30] too.

The  $\gamma_{\text{cpl},j}$  values for complexes-VacO in ALR's and the GB core do not differ within the error limits from the  $\gamma_{\text{vac},j}$  values for formation of vacancies in the crystallite volume and in the GB core respectively:

$$\gamma_{\text{cpl},j}/\gamma_{\text{vac},j} \cong 1.1 \pm 0.5. \quad (17)$$

Such ratio seems to be due to the absence of high frequency modes in LSCV, which are characteristic of interstitial impurities [31].

## 4. Conclusion

Formation enthalpies  $Q_{\text{cpl},1}$  of complexes-VacO in the core of large-angle common-type GB's in  $d$  transition metals having a BCC lattice (Cr, Ta and W) were measured for the first time. Formation enthalpies  $Q_{\text{vac},1}$  of vacancies in the core of large-angle common-type GB's in polycrystalline Cr, Ta and W were determined. Formation enthalpies  $Q_{\text{cpl},1}$  of the complexes-VacO in the GB core linearly depend on homologous temperatures  $\Lambda_{\text{cpl},1}$ . Empirical parameters  $(\beta, \alpha)_{i,j}$ , which characterize contributions of potential and vibration energies to formation enthalpies of vacancies ( $Q_{\text{vac},j}$ ) and complexes-VacO ( $Q_{\text{cpl},j}$ ) in the bulk of crystallites, ALR's and GB cores, were found. Dynamic contributions to formation enthalpies  $Q_{\text{vac},j}$  of vacancies in the lattice and the GB core and to formation enthalpies  $Q_{\text{cpl},j}$  of complexes-VacO in ALR's and the GB core were defined by the ratio  $(\beta/\alpha)_{i,j}$  of empirical parameters. Resonance low-frequency modes of LSCV of GB core atoms caused a several-fold decrease in the dynamic contributions to the enthalpies  $Q_{\text{vac},1}$  of vacancies and  $Q_{\text{cpl},1}$  of VacO complexes formed in the GB core.

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