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CRITICAL BEHAVIOUR OF GRAIN BOUNDARY DIFFUSION NEAR THE CURIE POINT IN IRON-SILICON ALLOY

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Abstract

The temperature dependence of bulk diffusion of zinc, tin and aluminium in a Fe-5% at Si alloy have been studied in the vicinity of the Curie point. Also, the temperature dependence of the diffusion coefficient of zinc on the tilt boundary 43° <100> has been studied in the same alloy. These temperature dependences exhibit a ferromagnetic anomaly of diffusion. The critical indices have been determined for the magnetic part of the free activation energy of diffusion. The treatment of the published and of our data has shown that this critical index is independent, within the accuracy of the experiments, of the type of diffusant /so-called "universality"/. The boundary diffusion critical index is markedly different from the bulk one, exceeding it by approximately a factor of 1.5. The Curie temperature is coincident in the bulk and one the boundary.

Experimental

Critical phenomena near kind II phase transitions in systems of low dimensionality are very intriguing for researchers.

Our goal was to study critical phenomena at grain boundaries near the ferromagnetic - paramagnetic state transformation by making use of diffusion.

We used Fe-5.0 at % Si bicrystals. This is a minimal amount of silicon that isolates the γ-region on the Fe-Si binary diagram and enables one to grow mono- and bicrystals with b.c.c. structure [1]. The Fe-5.0 at % Si alloy was prepared from armco-iron and silicon of semiconductor purity. The samples were grown by electron-beam zone melting in a vacuum of 10^{-6} torr, the growth rate being 1mm/min. The grain boundary diffusion was studied in a bicrystal with a tilt boundary ⟨100⟩ and misorientation angle of 43°. The misorientation angle was determined from etch pits and by optical orienting using a laser light source. The angle determination accuracy was 0.5°. For diffusional anneals a massive bicrystal was cut into samples of 8-12 mm in length and 1.5x1.5 mm in cross-section on an electric-spark machine. The boundary was in the middle normal to the long side of the sample. The diffusant (tin or zinc) was deposited on each sample by immersing it into the melt. The samples were encapsulated into evacuated quartz ampoules. The annealing temperature ranged from 660 to 975°C. The temperature was maintained with an accuracy of +0.5°C.

Following the anneal, the sample was mechanically ground and polished. The bulk diffusion coefficients were determined using electron probe microanalysis from the diffusion profiles taken away from the grain boundary, normal to the sample surface, along the ⟨100⟩ axis. The values of D were determined from 5-7 diffusion profiles using the expression

$$D = \frac{x^2}{4t[erf^{-1}(1-C/C_o)]} \qquad (1)$$

for the constant surface concentration, where t is the annealing duration, c is the concentration, C_o is the solubility limit. A quantitative analysis with all the necessary corrections was employed for the determination of the concentration from the electron probe microanalysis. To determine the boundary diffusion coefficients of zinc, we took a number of diffusion profiles across the boundary parallel to the sample surface with the deposited diffusant. The profiles were taken starting from the sample surface, the step being 10 μm. The product of the boundary diffusion coefficients, D', by the boundary diffusion width, δ, was determined by Fisher's formula

$$D'\delta = 2(D/\pi t)^{\frac{1}{2}} y^2/(\ln(C/C_o))^2 \qquad (2)$$

where c is a maximal concentration on the concentration profile, taken normal to the grain boundary at a depth y.

Results

Figs 1 and 2 present the temperature dependences of the bulk diffusion coefficients in Arrhenius coordinates. An accurate determination of the critical indices required a great number of the experimental points (2-3 times as much as in the works [2-9], where the diffusion coefficients were measured for iron or cobalt near the Curie point). In Figs 1 and 2 the temperature dependences exhibit clearly a "paramagnetic" Arrhenius straight line. In this portion the activation energy, E, and the preexponential factor, D_o, for tin and zinc are equal to E_{Sn} = 51±1 kcal/mol; D_{oSn} = 4±0.5 cm^2/S; E_{Zn} = 58±1 kcal/mol; D_{oZn} = 30±10 cm^2/S. Zinc, tin and silicon decrease the Curie point of Iron. In figs 1,2 the diffusion coefficients are presented for 0.23 at % tin and 0.98 at % zinc contents. From Figs 1 and 2 one can determine the Curie temperatures of these alloys (740±2°C for the alloy with zinc and with tin). Below these temperatures there are regions with high physically senseless values of the activation energy and of the preexponential diffusion factor.

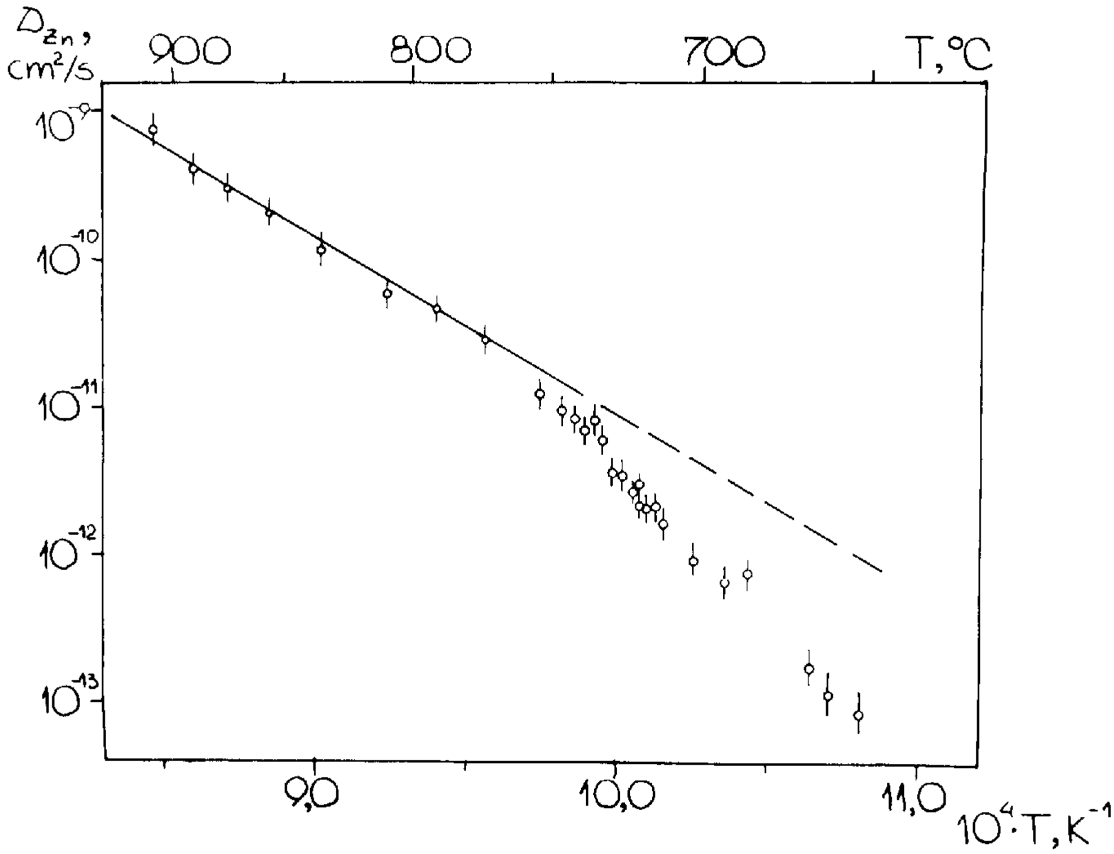

Figure 1. Temperature dependence of the bulk heterodiffusion coefficient of zinc in the alloy Fe-5 % Si.

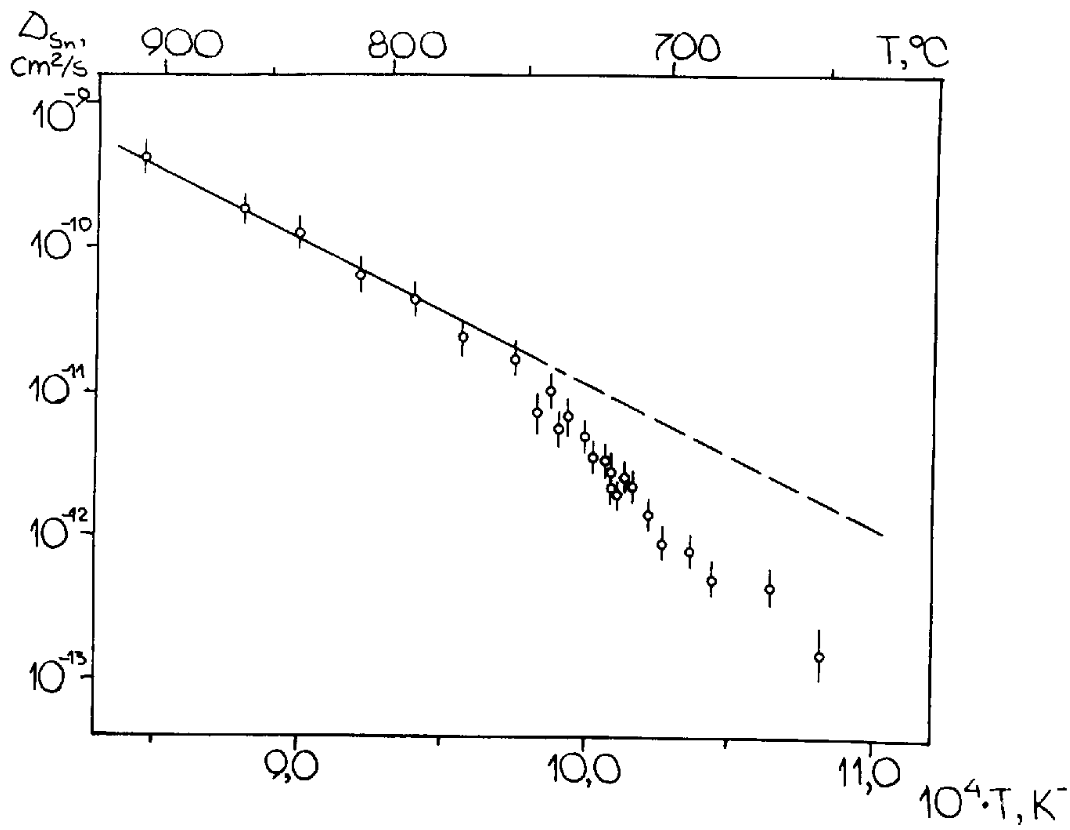

Figure 2. Temperature dependence of the bulk hetero-diffusion coefficient of tin in the alloy Fe-5 % Si.

Fig. 3 presents the temperature dependence of $D'\delta$ for the zinc diffusion across the tilt boundary <100> , the misorientation angle being 43±0.5°. Qualitatively, its form is similar to those of the temperature dependences of the bulk diffusion coefficients, shown in Figs 1 and 2. The temperatural anomaly of the boundary diffusion of substitutional atoms near the Curie point has been observed for the first time. The activation energy, E_b, and the preexponential factor, $D_o'\delta$, of the boundary diffusion equal: E_b = 42±3 kcal/mol, $D_o'\delta$ = 2±1 cm³/S. Thus, the value of E_b is 1.4 times smaller as compared with the bulk value. Below the Curie point the boundary diffusion coefficient decreases with the temperature more rapidly than the bulk one by approximately 1.6 times. We have verified the correctness of the determination of the $D'\delta$ value using Fisher's formula as an asymptotic form of Whipple's formula.

For this case the condition $\beta = D'\delta / D\sqrt{Dt} \gg 1$ must be fulfilled. In our case the temperature variation from 908 to 652°C leads to an increase of the β value from 14.7 to 191.

Discussion

The temperature dependence of the diffusion coefficient at a vacancy mechanism is given as

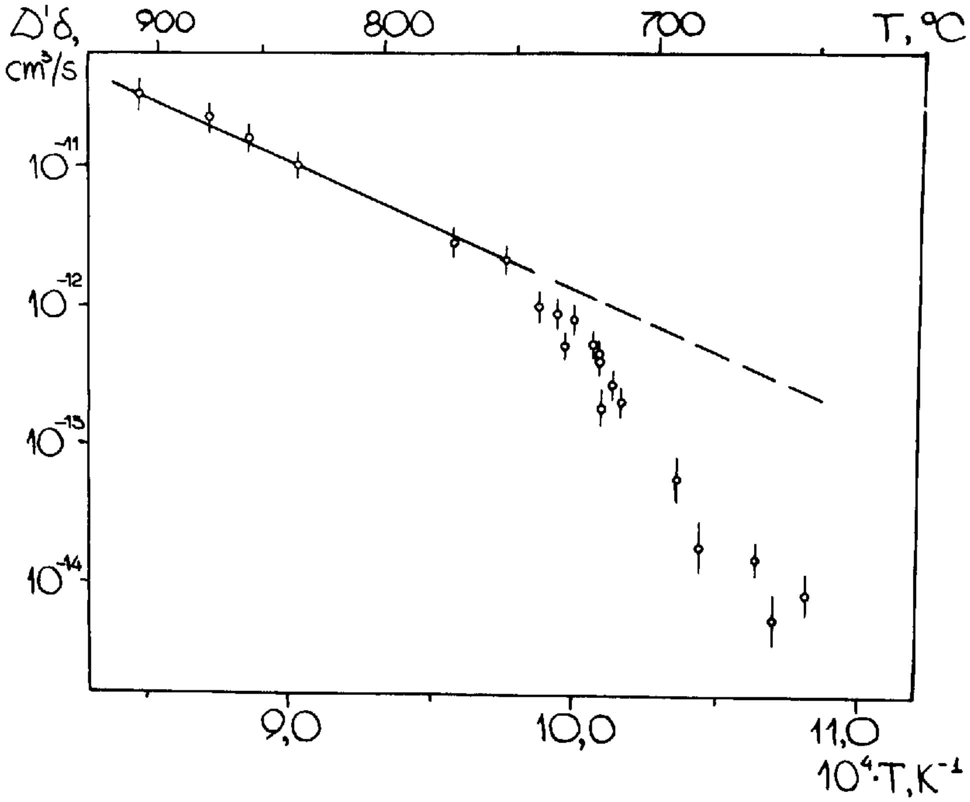

Figure 3. Temperature dependence of D'δ at zinc diffusion across the tilt boundary <100> , $\varphi = 43^{o}$, the alloy Fe-5 % Si.

$$D = gfa^2\nu \exp(-G/RT) \tag{3}$$

where g is the geometrical factor, f is the correlation factor, a is the lattice parameter, ν is the frequency of thermal oscillations of atoms, G is the free activation energy. We assume that the values of f and ν do not alter when transiting via the Curie point. The free activation energy involves the paramagnetic (index p) and magnetic (index m) components:

$$G = G_p + G_m = H_p - TS_p + G_m \tag{4}$$

here H_p and S_p are the enthalpy and enthropy of the diffusion activation.

The theory of critical phenomena [22] asserts that near the kind II phase transition the free energy derivatives (heat capacity, susceptibility etc) are temperature dependence according to the power law, for example

$$\chi \sim \left| \frac{T - T_c}{T_c} \right|^{-\gamma}$$

here γ is a so-called susceptibility critical index. Critical indices are an important characteristic of the system near the phase transitions. If in a three-dimensional case their values are independent of the system type, lattice structure etc, then two-dimensional objects fall into a number of so-called universality classes. We shall determine the critical indices for G_M and find out how they are associated with those for thermodynamical values and try to gain an understanding in physical causes of this interrelation.

We designate the critical index for G_M as d.

First we determine it for the diffusion data, known from the literature. To this end we plot $\Delta G_M/R$ vs $|T-T_c|/T_c$ in double logarithmic coordinates. Here

$$\Delta G_M = G_m(T) - G_m(T_c) \tag{5}$$

The calculation of d turned out possible from the four works:

System	Selfdiffusion in α-iron	Diffusion of zinc in α-iron	Diffusion of cobalt in α-iron	Selfdiffusion of iron in the alloy Fe-7.64 at % Si
reference	[3, 4]	[5]	[6]	[7]
	0.9±0.2	0.8±0.1	0.8±1	0.93±0.05

In Fig. 4 our data for the bulk diffusion coefficients of zinc are plotted in logarithmic coordinates. We have determined the Curie temperature from the maximal slope on the dependences lgD-T^{-1}. It makes up 740±2°C, this agrees with the data of [20]. The critical indices equal d_{Zn} = 0.8±0.1, d_{Sn} = 0.7±0.1.

So, the critical index for the magnetic part of the diffusion free activation energy is weakly dependent on the type of the diffusant and makes up 0.8-0.9. It can, therefore, be said that the critical behaviour of this value is universal.

Fig. 5 shows $\Delta G_M/R$ vs $|T-T_c|/T_c$ for the boundary diffusion of zinc. The Curie temperature, T_c, was also determined from a maximal slope on the dependence lgD'δ -1/T. It is consistent with the bulk one and is equal to 740±2°C. The critical index d_{gb} = 1.2+0.15, that exceeds the bulk value of d.

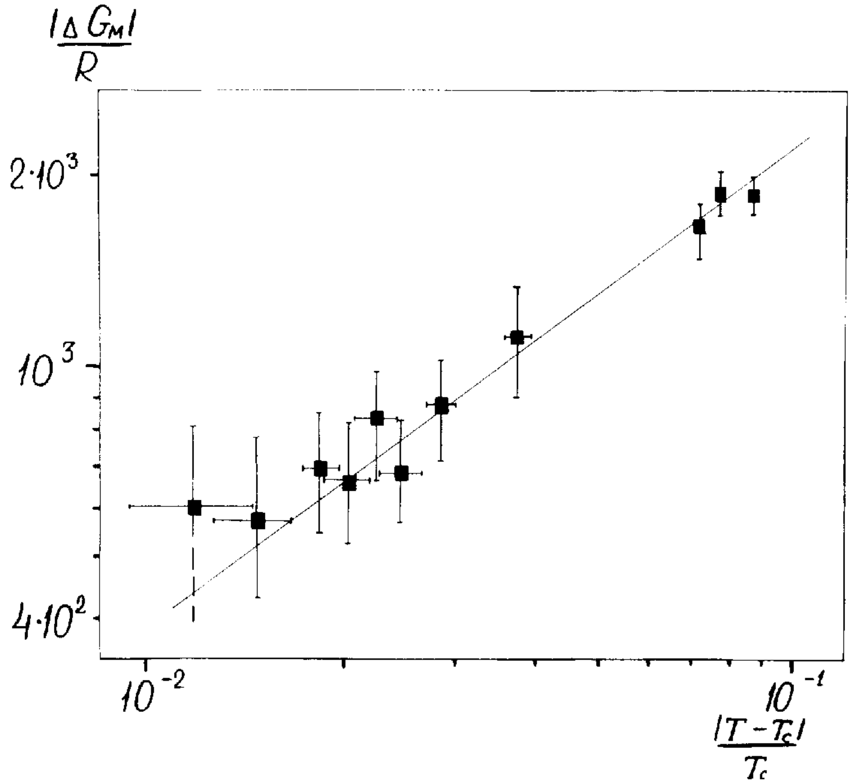

Figure 4. $\Delta G_M/R$ value vs $|T-T_c|$ in scaling coordinates for diffusion of zinc in Fe-5 % Si.

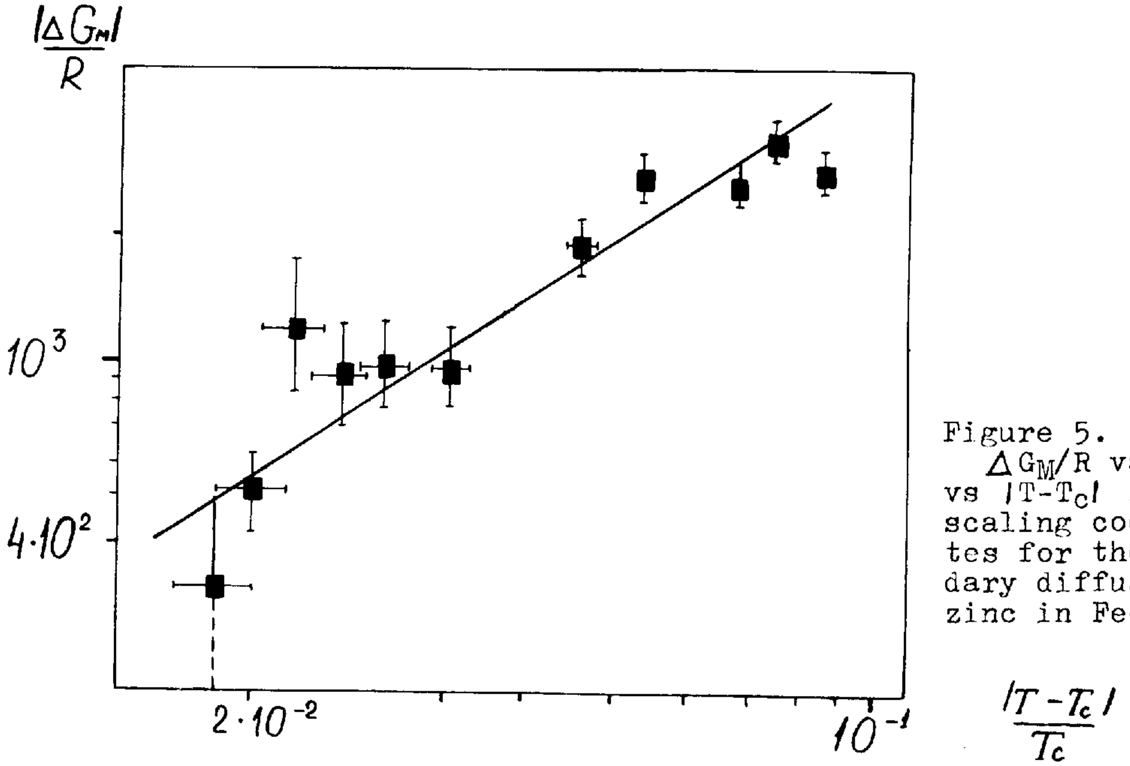

Figure 5. $\Delta G_M/R$ value vs $|T-T_c|$ in scaling coordinates for the boundary diffusion of zinc in Fe-5 % Si.

Table 1

Coefficient of the bulk diffusion of tin in the alloy Fe-5 at % Si

Temperature °C	Annealing duration t, hour	Coefficient of diffusion D_{Sn} cm^2/S
1	2	3
908	3.0	$4.2 \cdot 10^{-10}$
862	12.0	$1.9 \cdot 10^{-10}$
838	68.0	$1.3 \cdot 10^{-10}$
813	54.0	$6.6 \cdot 10^{-11}$
792	50.0	$4.6 \cdot 10^{-11}$
772	110.0	$2.5 \cdot 10^{-11}$
753	100.0	$1.8 \cdot 10^{-11}$
745	167.0	$7.4 \cdot 10^{-12}$
740	78.0	$1.1 \cdot 10^{-11}$
737	135.0	$5.9 \cdot 10^{-12}$
734	120.0	$7.2 \cdot 10^{-12}$
728	85.5	$5.2 \cdot 10^{-12}$
725	80.0	$3.8 \cdot 10^{-12}$
721	96.0	$3.6 \cdot 10^{-12}$
719	137.0	$3.0 \cdot 10^{-12}$
719	170.0	$2.3 \cdot 10^{-12}$
717	121.0	$2.1 \cdot 10^{-12}$
714	212.5	$2.8 \cdot 10^{-12}$
711	232.0	$2.4 \cdot 10^{-12}$
706	220.0	$1.5 \cdot 10^{-12}$
702	190.0	$9.5 \cdot 10^{-13}$
692	216.0	$8.5 \cdot 10^{-13}$
685	250.5	$5.4 \cdot 10^{-13}$
667	282.0	$4.7 \cdot 10^{-13}$
652	816.0	$1.6 \cdot 10^{-13}$

Table 2

Parameters of the bulk and grain boundary diffusion of zinc in the alloy Fe-5 at % Si

Temperature ^{o}C	Annealing duration t, hour	Bulk diffusion coefficient, D_{Zn}, cm^2/S	$D'\delta$ cm^3/S gentle portion	$D'\delta$ cm^3/S steep portion
1	2	3	4	5
908	3.0	$7.6\cdot10^{-10}$	$(3.2+0.8)\cdot10^{-11}$	2
890	2.0	$4.1\cdot10^{-10}$	$(4.0+1.2)\cdot10^{-11}$	$2\cdot10^{-13}$
875	5.5	$3.1\cdot10^{-10}$	$(2.2\pm0.5)\cdot10^{-11}$	$2\cdot10^{-13}$
857	7.5	$2.1\cdot10^{-10}$	$(1.6+0.4)\cdot10^{-11}$	$3\cdot10^{-13}$
836	13.0	$1.2\cdot10^{-10}$	$(1.0\pm0.3)\cdot10^{-11}$	
809	21.0	$6.2\cdot10^{-11}$		
790	63.0	$4.9\cdot10^{-11}$		
772	110.0	$3.0\cdot10^{-11}$	$(2.8\pm0.5)\cdot10^{-12}$	
753	100.0	$1.3\cdot10^{-11}$	$(2.2\pm0.5)\cdot10^{-12}$	$3\cdot10^{-15}$
745	167.0	$1.0\cdot10^{-11}$		
740	78.0	$8.9\cdot10^{-12}$	$(1.0\pm0.3)\cdot10^{-12}$	
737	135.0	$7.4\cdot10^{-12}$		
734	120.0	$8.3\cdot10^{-12}$	$(9.1\pm1.0)\cdot10^{-13}$	
731	95.0	$6.3\cdot10^{-12}$	$(5.4+0.8)\cdot10^{-13}$	1.10^{-13}
728	85.5	$3.8\cdot10^{-12}$	$(8.3+0.8)\cdot10^{-13}$	
725	80.0	$3.6\cdot10^{-12}$		
721	96.0	$2.8\cdot10^{-12}$	$(5.5\pm0.7)\cdot10^{-13}$	
719	137.0	$2.3\cdot10^{-12}$	$(4.7\pm0.6)\cdot10^{-13}$	
719	170.0	$3.2\cdot10^{-12}$	$(4.0\pm0.6)\cdot10^{-13}$	$1\cdot10^{-15}$
717	121.0	$2.2\cdot10^{-12}$	$(1.9\pm1.0)\cdot10^{-13}$	
714	212.5	$2.3\cdot10^{-12}$	$(2.8\pm0.6)\cdot10^{-13}$	
711	232.0	$1.7\cdot10^{-12}$	$(2.2\pm0.5)\cdot10^{-13}$	
702	190.0	$9.8\cdot10^{-13}$		$4\cdot10^{-16}$
692	216.0	$6.9\cdot10^{-12}$	$(6\pm3)\cdot10^{-14}$	$3\cdot10^{-16}$
685	250.5	$8.1\cdot10^{-12}$	$(2\pm1)\cdot10^{-14}$	
667	282.0	$1.8\cdot10^{-13}$	$(1.6\pm0.4)\cdot10^{-11}$	
662	240.0	$1.2\cdot10^{-13}$	$(6\pm3)\cdot10^{-15}$	
652	816.0	$9.1\cdot10^{-14}$	$(9\pm2)\cdot10^{-15}$	

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