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Residual resistivity of interstitial and substitutional impurities in transition metals

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Abstract. Residual resistivities for interstitial H in the face-centred cubic metals Cu, Ag, Ni, Pd and Al as well as in the body-centred cubic metals V, Nb and Ta are calculated using the Korringa–Kohn–Rostoker Green function description of Bloch electron scattering by impurity clusters. Heavier interstitials like B and C in Pd and C and O in Nb are also investigated. Inclusion of environmental effects, especially local lattice deformation of the first shell of surrounding atoms, turned out to be of crucial importance in order to obtain agreement with experimental residual resistivities. The firmly established absence of a H/D isotope effect in Pd, V, Nb and Ta can be explained. Measured residual resistivities due to substitutional impurities in Cu, Ag, Pd, Al and Nb are reproduced with varying success, depending on the complexity of the electronic structure of the defect potential. A first shell of surrounding metal atoms improves the calculated results, while lattice distortion is not as important as it is for the interstitial alloys.

1. Introduction

The resistivity change per atomic per cent of an impurity in a metal, $\Delta\rho$, can be measured accurately. Absolute experimental errors are usually within $\pm 0.1 \mu\Omega \text{ cm/at.}\%$, while the resistivity changes themselves vary from $0.1 \mu\Omega \text{ cm/at.}\%$ to values larger than $10 \mu\Omega \text{ cm/at.}\%$ for substitutional impurities like Cr and Zr in Cu [1]. Well established values for $\Delta\rho$ can, for instance, be used to obtain (time-dependent) impurity concentration profiles along a sample [2–4]. In such experiments, where the formation and the relaxation of a concentration gradient yields information on the diffusion coefficient and possibly on the electromigration effective valence of impurities in the metal, the temperature is finite. At zero temperature the resistivity change per atomic per cent in dilute metal–impurity systems is termed the residual resistivity and is denoted by ρ_0 .

At temperatures where the coupling of lattice vibrations to oscillating impurities is negligible, the residual resistivity turned out to be accessible by theoretical and computational means. Once the characteristics of the electron–impurity scattering are available in terms of a vector field of mean free paths over the Fermi surface, ρ_0 can readily be calculated. Coleridge [5] studied the scattering of electrons by Ni, Fe and Al in Cu. In a series of papers Mertig *et al* [6–8] applied the Korringa–Kohn–Rostoker (KKR) Green function method to the description of substitutional-impurity scattering in metals

and used it to describe the electronic structure of Cu(X) where X stands for a wide variety of impurity elements. The calculated results for fourth-row impurities in Cu are in good agreement with experimental data while the results for fifth-row impurities in some cases deviate strongly from measured data.

The calculations mentioned above included d-partial-wave scattering but did not account for charge-transfer effects and local lattice distortion. An attempt to estimate the influence of such effects on residual resistivities in Cu and Ag has been made via a finite cluster model [1]. It turned out that even the inclusion of lattice distortion and charge transfer, the latter being present in the self-consistent potentials [9] used, is not to be expected to yield large improvement. In general the finite cluster resistivities agreed with experiment as well as or, in some cases, even better than the ones including the host band structure. De Ruiter *et al* [10] showed in a pseudopotential study of substitutional impurities in In that long-range strain fields around defects influence ρ_0 to some extent.

Recently a computer program able to treat interstitial impurities with one or two surrounding shells in FCC metals has become available [11]. In order to account properly for lattice distortion, angular momenta up to $l = 3$ had to be included. A direct solution of the set of algebraic equations, derivable from the Boltzmann transport equation, according to Sondheimer [12] had to be replaced by an iterative procedure to solve the Boltzmann equation. Unfortunately an incorrect factor for the conversion from atomic units to $\mu\Omega \text{ cm/at. \%}$ meant that all results in [11] should be multiplied by a factor of 2.

In this paper the KKR Green function method will be employed to calculate residual resistivities for interstitial and substitutional impurities in FCC and BCC metals. Both the effect of local lattice deformation as well as charge transfer in the impurity cluster are accounted for in the calculations to be presented in this paper. The results will be compared with available experimental data. From this comparison it should be possible to judge the quality of the muffin-tin (MT) potential describing the defect electronic structure. Because of the relative accuracy of the experimentally available resistivity changes it can be stated that, when theory and experiment match, the electron-impurity scattering in the system is described satisfactorily.

In section 2 the expressions resulting from the application of the KKR Green function formalism to the Boltzmann equation for electron transport will be presented. In section 3 the potentials used for the various systems will be discussed briefly. Sections 4 to 7 present results obtained for various FCC and BCC metals with both interstitial and substitutional impurities. For clarity we remark that the main guidance in choosing the systems was their occurrence in the research on electromigration as described in [13] and [14]. In section 8 the results will be discussed and several conclusions are formulated.

Atomic units such that $\hbar = 2m = 1$, m being the electron rest mass, are used. As a consequence $e^2 = 2$, where $e = |e|$ is the elementary charge.

2. Expression for the vector mean free path

The problem of the conductivity of an electron gas containing randomly distributed impurities at a low density can be treated within Kubo's linear response formalism [15]. The resulting conductivity σ to lowest order in the impurity concentration equals the conductivity obtained in solving the linearized Boltzmann equation. In a real metal-

impurity system one seeks the solution g_k of the linearized Boltzmann equation for elastic scattering

$$e \left(\frac{\partial f_0(\varepsilon_k)}{\partial \varepsilon_k} \right) \mathbf{v}_k \cdot \mathbf{E} = \sum_{k'} P_{kk'} (g_k - g_{k'}). \quad (1)$$

The function g_k denotes the deviation from the equilibrium distribution function $f_0(\varepsilon_k)$. $P_{kk'}$ gives the transition probability per unit time for an electron being scattered elastically from Bloch state $|k\rangle \equiv |n\mathbf{k}\rangle$ into $|k'\rangle \equiv |n'\mathbf{k}'\rangle$ at energy $\varepsilon_k = \varepsilon_{k'}$. In (1) \mathbf{v}_k denotes the group velocity of an electron in state $|k\rangle$.

When g_k is assumed to be linear in the external electric field \mathbf{E} , it obtains the form

$$g_k = e(\partial f_0(\varepsilon_k)/\partial \varepsilon_k) \Lambda_k \cdot \mathbf{E} \quad (2)$$

with $\partial f_0/\partial \varepsilon = -\delta(\varepsilon - \varepsilon_F)$ at $T = 0$. Equation (1) can then be written as

$$\Lambda_k = \tau_k^0 \left(\mathbf{v}_k + \sum_{k'} P_{kk'} \Lambda_{k'} \right) \quad (3)$$

and has to be solved for the vector field Λ_k , termed the vector mean free path. The electron-impurity lifetime τ_k^0 is given by

$$\frac{1}{\tau_k^0} = \sum_{k'} P_{kk'} = -2c \operatorname{Im} T_{kk}. \quad (4)$$

The second equality in (4) is the optical theorem connecting diagonal elements of the transition matrix, T_{kk} , to a sum over all transition probability rates for scattering out of state $|k\rangle$. The transition probability per unit time for a low impurity fraction c of the total number of atoms N is given by

$$P_{kk'} = 2\pi c N |T_{kk'}|^2 \delta(\varepsilon_k - \varepsilon_{k'}). \quad (5)$$

The current density in the metal sample (volume Ω) is given by the volume averaged sum over all contributions $-e\mathbf{v}_k$ of electrons in states $|k\rangle$ weighted by the deviation from equilibrium

$$\mathbf{j} = \frac{2}{\Omega} \sum_k -e\mathbf{v}_k g_k = \frac{2e^2}{\Omega} \sum_k (\mathbf{v}_k \times \Lambda_k) \delta(\varepsilon_k - \varepsilon_F) \mathbf{E}. \quad (6)$$

Comparing with $\mathbf{j} = \boldsymbol{\sigma} \mathbf{E} = \boldsymbol{\rho}^{-1} \mathbf{E}$ and converting the summation into an integration over the Fermi surface gives

$$\boldsymbol{\rho}^{-1} = \frac{2e^2}{(2\pi)^3} \int_{\text{FS}} dS_k \hat{\mathbf{v}}_k \times \Lambda_k \quad (7)$$

with $\hat{\mathbf{v}}_k = \mathbf{v}_k/v_k$.

Within the KKR Green function formalism the t -matrix elements for electron-impurity scattering can be expressed as

$$T_{kk'} = \sum_{\substack{nLL' \\ n'L'}} C_{nL}^*(k) T_{LL'}^n A_{nL'n'L'} C_{n'L'}(k'). \quad (8)$$

The wavefunction coefficients $C_{nL}(k)$ are labelled by an index n numbering the atoms in the impurity cluster and by $L \equiv (l, m_l)$, a combined angular momentum index. These

coefficients as well as the back-scattering matrix A are discussed in great detail elsewhere [16–18]. The cluster t -matrix with elements ($\kappa \equiv \sqrt{\varepsilon_F}$)

$$T_{LL'}^n = -(1/\kappa)J_{LL'}(-\Delta_n) \sin(\bar{\eta}_l^n - \eta_l^n) \exp[i(\bar{\eta}_l^n - \eta_l^n)] \quad (9)$$

contains the phaseshifts for the MT potentials in the impurity cluster in the present ($\bar{\eta}_l^n$) and in absence (η_l^n) of the impurity. Lattice distortion at site n is accounted for through the matrix $J(\Delta_n)$ with Δ_n a small displacement vector. The matrix elements of $J(\Delta)$ are given in terms of Gaunt coefficients $C_{LL'L'}$, spherical Bessel functions $j_l(\kappa\Delta)$ and real spherical harmonics $Y_L(\hat{\Delta})$

$$J_{LL'}(\Delta) = 4\pi i^{l-l'} \sum_{L''} i^{l''} C_{LL'L''} j_{l''}(\kappa\Delta) Y_{L''}(\hat{\Delta}). \quad (10)$$

The kernel in the integral equation (3) for the mean free path is degenerate. This can be made explicit upon substitution of equation (8) in (5)

$$P_{kk'} = 2\pi cN \sim \delta(\varepsilon_k - \varepsilon_{k'}) \sum_{\substack{nL \\ n'L'}} C_{nL}^*(k) C_{n'L'}(k) Q_{nL}(k') Q_{n'L'}^*(k') \quad (11)$$

with

$$Q_{nL}(k) \equiv \sum_{L'} T_{LL'}^n \sum_{n'L''} A_{nLn'L''} C_{n'L''}(k). \quad (12)$$

Microscopic reversibility demanding that $P_{kk'} = P_{k'k}$ can be demonstrated through careful rearrangement of factors in (11) combined with (12). The equation for the vector mean free path can be rewritten as

$$\Lambda_k = \tau_k^0 \left(v_k + 2\pi cN \sum_{\substack{nL \\ n'L'}} I_{nLn'L'} Q_{nL}(k) Q_{n'L'}^*(k) \right). \quad (13)$$

The vectorial matrix I is an integral over the Fermi surface with matrix elements [11]

$$I_{nLn'L'} = \frac{1}{V_{BZ}} \int_{FS} \frac{dS_k}{v_k} C_{nL}^*(k) \Lambda_k C_{n'L'}(k) \quad (14)$$

which shows that, apart from the vector mean free path, the integrand is composed of *host* wavefunction coefficients. The volume of the Brillouin zone is denoted by V_{BZ} and equals 4 or 2 in units of $(2\pi/a)^3$, a being the lattice constant, for FCC and BCC metals respectively.

Computer programs to calculate the residual resistivity of interstitial impurities at the octahedral and tetrahedral sites in FCC metals, the tetragonally distorted tetrahedral site in BCC metals and of substitutional impurities in FCC and BCC metals, have been designed. The Ziman approximation for the vector mean free path [19]

$$\Lambda_k^{\text{Ziman}} = v_k \left(\frac{1}{V_{BZ}} \int_{FS} \frac{dS_{k'}}{v_{k'}} (1 - \hat{v}_k \cdot \hat{v}_{k'}) P_{kk'} \right)^{-1} \quad (15)$$

is used as a starting point in the iterative solution of the Boltzmann equation. Again, integrals of the type (14) have to be calculated but now with Λ_k replaced by \hat{v}_k . The $Q_{nL}(k)$ in equation (12) can be calculated once and for all, given a metal-impurity system and a mesh of k -points over the Fermi surface. Manipulations such as the numerical integration over the Fermi surface and the multiplication of numerous k -dependent

matrices are well suited for treatment by the vector processor of the Cyber 995E computer used in the present investigations.

With the vector mean free path in the Ziman approximation as an initial guess, convergence of the mean free path in a sense that

$$\max_{k \in \text{FS}} \left(\frac{|\Lambda_k^{i+1} - \Lambda_k^i|}{|\Lambda_k^i|} \right) < 10^{-3} \quad (16)$$

where two subsequent iterations are numbered by i and $i + 1$, was attained in typically 4–10 iterations. At this point the residual resistivity had always converged to an accuracy better than the smallest experimental error ($\sim 0.05 \mu\Omega \text{ cm/at. \%}$). The differences between the Ziman approximation and the converged results for the residual resistivity are generally found to be small, as already noticed by Coleridge [5].

The optical theorem (equation (4)) was fulfilled exactly for embedded impurity clusters when lattice distortion is absent. This shows that the integrations over the Fermi surface are performed with great accuracy. When lattice distortion was admitted, the root-mean-square deviation from the optical theorem

$$\left\{ \sum_{\substack{\text{FS} \\ \text{mesh}}} \left[\left(\frac{1}{V_{\text{BZ}}} \int_{\text{FS}} \frac{dS_{k'}}{v_{k'}} P_{kk'} / (-2c \text{Im } T_{kk}) \right) - 1 \right]^2 / \sum_{\substack{\text{FS} \\ \text{mesh}}} 1 \right\}^{1/2} \quad (17)$$

was of order 10^{-7} to 10^{-4} depending on lattice distortion. This small deviation can be understood from the different occurrence of the matrix $J(\Delta)$ in the two factors of (17). This matrix accounts for lattice distortion through an expansion in terms of Bessel functions. A possible truncation error in this expansion due to the angular momentum cut-off at $l = 3$ is quadratically present in $P_{kk'}$ while in $-2c \text{Im } T_{kk}$ it occurs linearly.

3. Potentials

Among the MT potentials describing the metal–impurity systems in this study are those used in calculating the electromigration wind valence in [13] and [14]. In addition potentials with a smaller MT radius of the host metal atoms (and thus a larger radius for the interstitial) are used for some FCC metals containing interstitial impurities. A detailed description of the construction of the MT potentials has been given elsewhere [13, 17]. Here it is only mentioned that the host potentials are constructed starting from relativistic atomic charge densities, obtained from a Hartree–Fock–Dirac–Slater calculation [20] on atoms with a given electronic configuration.

Impurity potentials, constructed in a similar way, are made to satisfy a generalized Friedel sum rule [17, 21], which assures that the total electronic charge difference due to the impurity is accounted for. This is accomplished through a procedure whereby the MT potentials are shifted by a small constant potential up or down the energy scale. Such an energy shift slightly alters the scattering properties of a MT potential. Resulting changes in the charge density around the MT potential are usually interpreted as a change in the amount of screening associated with the potential [22]. In the interstitial systems the MT radii of the host and the interstitial atoms correspond to an interstitial MT sphere touching the atoms in the first surrounding shell. Fulfilment of the Friedel sum rule in these cases was obtained by shifting only the potentials of the first-shell atoms, all with the same amount of energy. The interstitial potential itself was always left unaltered. On the one hand, it is unphysical to accommodate large amounts of screening charge

Table 1. Residual resistivities in $\mu\Omega$ cm/at. % for interstitial impurities H, B and C at the octahedral site in FCC metals. Column 2 shows calculated values for a single interstitial in a perfect host. Columns 3 to 9 display calculated ρ_0 values as a function of the lattice deformation Δ , as a percentage of a , of the first shell. The last two columns show available experimental information.

System	ρ_0								Experimental	
	Imp. only	0%	0.5%	1%	1.5%	2%	2.5%	3%	ρ_0	Δ (%)
Cu(H)	1.68	1.80	1.83	1.86	1.90	1.95			1.50	
	2.66	2.71	2.76	2.81	2.87	2.94	3.02	3.09		
Ag(H)	2.11	2.11	2.15	2.19	2.24	2.30			1.34	
Ni(H)	0.001	0.54	0.60	0.75	0.88	1.06			0.67	
Pd(H)	0.001	0.30	0.39	0.52	0.68	0.88			0.32	1.0
	0.002	0.22	0.35	0.54	0.80	1.05				
Pd(B)	0.03	1.55		1.78	1.91	2.08	2.26	2.45	2.05	2.7
	0.10	2.48		2.83		3.43	3.72	4.02		
Pd(C)	0.07	1.77		2.13	2.32	2.58	2.86	3.21	2.7, 3.8	2.0
	0.26	3.14		3.38		3.79	3.94	4.07		
Al(H)	0.05	0.09	0.08	0.08	0.08	0.08				

Table 2. Calculated residual resistivities in $\mu\Omega$ cm/at. % for interstitial H at the tetrahedral site of FCC metals. Column 2 shows calculated values for a single interstitial in a perfect host. Columns 3 to 6 display calculated ρ_0 values as a function of the lattice deformation of the first shell.

System	ρ_0				
	Imp. only	0%	1%	2%	3%
Cu(H)	0.85	0.97	1.02	1.07	1.14
Ag(H)	1.32	1.57	1.65	1.73	1.82
Pd(H)	0.013	0.26	0.38	0.56	0.91
Al(H)	0.07	0.13	0.11	0.11	0.12

on the interstitial by shifting its potential rigidly by a large constant energy while, on the other hand, in test calculations the Friedel sum was found to be rather insensitive to the shift applied to interstitial hydrogen.

The strategy for shifting the potentials of the substitutional systems essentially amounts to using a single constant energy shift for all the atoms in the impurity cluster.

4. Results for interstitials in FCC metals

Tables 1 and 2 compile calculated residual resistivities, converged in the sense of the inequality (16), for several metal-impurity systems. These tables deal with impurities at the octahedral and at the tetrahedral site respectively. In these tables the first column

Table 3. Lattice constant a and the interstitial MT radii at the octahedral and tetrahedral (R_{MT}^i) sites pertaining to the host MT radius (R_{MT}^{host}) are given in Bohr. The Fermi energies ϵ_F corresponding to the different R_{MT}^{host} are in Ryd.

Metal	a	R_{MT}^{host}	R_{MT}^i		ϵ_F
			Octahedral	Tetrahedral	
Cu	6.831	2.415	1.003	0.543	0.584
		2.220	1.195	0.738	0.634
		2.049	1.366	0.909	0.627
Cu SCP	6.76	2.39			0.630
Ag	7.722	2.730	1.351	0.834	0.527
Ni	6.694	2.176	1.171	0.723	0.649
Pd	7.351	2.389	1.286	0.794	0.515
		2.205	1.470	0.978	0.577
Al	7.623	2.478	1.334	0.823	0.626
V	5.713	1.916	0.941	1.278	0.782
Nb	6.238	2.441			0.729
		2.092	1.027	1.395	0.852
Ta	6.238	2.092	1.027	1.395	0.927

of ρ_0 values shows the outcome from a calculation neglecting charge transfer to and lattice distortion of the first shell of surrounding atoms. In this case the Friedel sum rule is not satisfied, for the interstitial impurity potential was always left unshifted [13, 23]. The subsequent columns show ρ_0 as a function of the radial outward deformation of the first shell of perturbed host atoms. The Friedel sum rule was made to equal the number of valence electrons of the impurity by applying a constant energy shift to the MT potentials in the first shell. The last two columns give experimental data, if available. Whenever there are two lines of resistivities present, the first line corresponds with the description utilizing a larger MT sphere for the host. The second line corresponds with a somewhat smaller host-MT radius but a consequently larger MT radius for the interstitial. Table 3 summarizes the different MT radii for the host and for the interstitial along with Fermi energies and lattice constants.

In the interstice in FCC metals the two sites with highest point-group symmetry are the octahedral (point group O_h) and the tetrahedral (T_d) positions. Commonly the octahedral site surrounded by a first shell of six metal atoms is believed to be the equilibrium position for small interstitials. The second shell of eight atoms around the octahedral site was shown to be of only minor influence on the residual resistivity [11] and therefore will not be considered. The tetrahedral site is surrounded by four equivalent metal atoms.

4.1. Cu(H) and Ag(H)

It is seen in Cu and Ag that the addition of a first shell of host atoms, with or without lattice distortion, does not influence the hydrogen residual resistivity much. This means

that the electrons in Cu and Ag are most strongly scattered by the impurity itself, its surrounding being not too important. This was noted earlier from a comparison of the influence of the first shell on de Haas–van Alphen (dHvA) scattering quantities in Cu(H) and Pd(H) [24]. In Pd the electron–impurity scattering could only be calculated correctly upon explicit inclusion of the first shell while in Cu a (single site) average t -matrix approximation already gave reasonable results [25]. Enlargement of the MT sphere of the octahedral hydrogen atom in Cu from 1.195 to 1.366 Bohr, thereby decreasing the host MT radius, resulted in overall larger values for ρ_0 by a factor of approximately 1.5 (see table 1). This is in agreement with the above-mentioned behaviour because a larger interstitial implies a stronger scatterer. The smaller interstitial MT radius, corresponding to $0.175a$, resulted in ρ_0 values still exceeding the experimental result [26] $\rho_0 = 1.50 \mu\Omega \text{ cm/at.}\%$. At the tetrahedral site in Cu the resistivity is again smaller simply because of the smaller MT radius for the proton. A host MT radius corresponding to touching spheres resulted in values of 1.20 and $1.34 \mu\Omega \text{ cm/at.}\%$ for the single hydrogen and the complete impurity cluster respectively. In this case there is no possibility to account for lattice distortion. The sensitivity to the choice of the MT radii is observed for other systems as well and will be returned to in the concluding section.

In Ag an interstitial MT radius of $0.175a$ at the octahedral site leads to values much larger than the measured value [27]. At the tetrahedral site a calculation including the first shell does give resistivities in better agreement with experiment. In a previous publication [11] this site was ruled out as a possible equilibrium position for hydrogen or deuterium in Ag. This conclusion was founded on erroneous results and has to be rejected.

From the results for Cu(H) and Ag(H) it is learned that a hydrogen atom in these metals constitutes a very strong scatterer, regardless of the precise environmental details. It is as if the Cu and Ag lattices could be replaced by a jellium with the correct Fermi energy, still imposing bounds on the MT radius of the impurity via their lattice constants. The actual free-electron values of ρ_0 can be obtained from the famous expression of Friedel [28]

$$\rho_0 = \frac{4\pi}{Z_h e^2 \varepsilon_F^{1/2}} \sum_l (l+1) \sin^2(\bar{\eta}_{l+1}^I - \bar{\eta}_l^I) \quad (18)$$

where Z_h is the host valence (i.e. 1 for Cu and Ag) and $\bar{\eta}_l^I$ are the same hydrogen phase shifts as used in table 1 ($R_{\text{MT}}^I = 0.175a$). One then finds the values $2.98 \mu\Omega \text{ cm/at.}\%$ and $3.54 \mu\Omega \text{ cm/at.}\%$ for Cu(H) and Ag(H) respectively.

4.2. Ni(H), Pd(H), Pd(B) and Pd(C)

The residual resistivity in Ni(H) was measured at 4.2 K [27] where Ni is in its ferromagnetic phase ($T_C = 627 \text{ K}$). In this work Ni is treated as a paramagnetic metal and it is therefore interesting that the calculated ρ_0 agrees so well with experiment at about 0.75% lattice distortion. This can be understood from the fact that at the Fermi energy the density of states (DOS) for the minority spin is much greater than that of the majority spin. The DOS and the dispersion relation of paramagnetic Ni and of the minority spin in ferromagnetic Ni are much alike [29]. If the electron–impurity scattering is assumed to be spin-independent, it is then not completely surprising that a paramagnetic Ni host gives a good description.

Both in Ni(H) and in Pd(H) the influence of the perturbed surrounding atoms is astonishing (see table 1). Lattice distortions are deduced from relative volume changes

per unit concentration [30]. At 1% lattice distortion the residual resistivity is increased by factors of 750 and 520 respectively ($R_{\text{MT}} = 0.175a$). The residual resistivity due to the hydrogen alone is negligible! As a consequence a larger MT radius ($R_{\text{MT}} = 0.2a$) for H in Pd does not alter the results as much as was the case for the Cu(H) system. At a lattice distortion of about 1% the difference vanishes. In Pd(H) agreement with the measured resistivity is reached between 0% and 0.5% lattice distortion for the smaller as well as for the larger MT radius.

At the tetrahedral site (see table 2) in Pd hydrogen constitutes a stronger scatterer. The resistivity due to the hydrogen alone is a factor of 13 larger than that at the octahedral site, in spite of its smaller MT radius (see table 3). Total cluster values, however, are smaller.

Heavier impurities in Pd, such as B and C, again are weak scatterers by themselves. Only inclusion of the first shell surrounding the octahedral site makes that the calculated ρ_0 become comparable with experimental results. For Pd(B) the smaller interstitial MT radius clearly gives the best agreement with experiment. At 2% lattice distortion, which is below the experimental value [17] of 2.7%, the measured results of Cadeville and Lerner [31] are reproduced. An amusing situation exists for Pd(C). At 2% lattice distortion [17] the experimental residual resistivity of Cadeville and Lerner [31] compares nicely with the value obtained in using the smaller interstitial MT radius. The result of Bakker *et al* [32] is in fine agreement with a spatially more extended carbon potential, at the same lattice distortion.

4.3. Al(H)

Neither the residual resistivity nor the lattice deformation due to the proton in Al are known. Effective-medium calculations for Al(H) by Puska and Nieminen [33] indicate a lattice distortion of the first shell of approximately 1.6% at the octahedral site and 3.4% at the tetrahedral site.

From tables 1 and 2 it is seen that lattice distortion does not influence ρ_0 in a systematic way. Inclusion of the first shell enhances the residual resistivity by a factor of almost 2 with respect to hydrogen alone. Compared with the other resistivities (first shell included) in tables 1 and 2, ρ_0 is small (0.08 to 0.13 $\mu\Omega$ cm/at. %).

This low resistivity increase is surprising, for Al is a trivalent simple metal. One might expect formula (18) to give a result comparable with the above-mentioned values. This is not the case at all. The Friedel expression for ρ_0 gives 1.02 $\mu\Omega$ cm/at. %.

In search of an explanation for this unexpectedly low residual resistivity additional finite cluster calculations [34] have been performed. In such a calculation the impurity cluster consists of the same cluster potential as was used in the real-metal calculation. The crystal potential, however, has been replaced by a constant potential, the MT zero of the host metal. One then finds a resistivity of $\rho_0 = 0.64 \mu\Omega$ cm/at. % at 0% lattice distortion. Replacement of the first-shell atoms by Al host atoms leads to $\rho_0 = 0.66 \mu\Omega$ cm/at. %, which is to be compared with the impurity-only result for Al(H) in table 1. These values still differ appreciably from those given in table 1.

From a comparison of the host wavefunction around the interstitial site

$$\Psi_k(\mathbf{x} + \mathbf{R}_l) = \sum_L C_{lL}(k) j_L(\mathbf{x}) \quad (19)$$

with the well known plane-wave expansion

$$e^{i\mathbf{k} \cdot (\mathbf{x} + \mathbf{R}_l)} = 4\pi e^{i\mathbf{k} \cdot \mathbf{R}_l} \sum_L i^l Y_L(\hat{\mathbf{k}}) j_L(\mathbf{x}) \quad (20)$$

one finds that for free-electron metals it holds that

$$C_{iL}(k) = (4\pi/\Omega^{1/2}) e^{ik \cdot R_i} i^l Y_L(\hat{k}). \quad (21)$$

Here x is a coordinate centred around the interstitial site R_i and Ω is the unit-cell volume. The spherical wave $j_L(x)$ is the product of a real spherical harmonic $Y_L(\hat{x})$ and a spherical Bessel function $j_L(\sqrt{\varepsilon_F}x)$. In Al equation (21) was obeyed quite well over large parts of the Fermi surface when compared with Cu, Ag and especially with the situation in Pd. In this way complete failure of the free-electron approximation in the interstitial region in Al could be ruled out.

The ultimate cause of the low ρ_0 value for the Al(H) system was found in the remarkably strong influence of back-scattering by the Al crystal. To this end the A -matrix describing the effect of back-scattering [17, 18] was set equal to $\mathbf{1}$, the unit matrix. This means that all multiple scattering effects in electron impurity scattering are neglected. Residual resistivity calculations in Al(H) with $A = \mathbf{1}$ resulted in $\rho_0 = 0.49 \mu\Omega \text{ cm/at.}\%$ for the impurity cluster at 0% lattice deformation. This value is a factor of 5.44 larger than the corresponding value in table 1. In Cu(H) and Ag(H) ρ_0 increased by factors of only 1.12 and 1.35 upon taking $A = \mathbf{1}$. The fact that in the finite cluster calculations on Al(H) relatively large values of ρ_0 were also found demonstrates that the octahedral seven-atom cluster embedded in a constant potential does not provide an adequate description of the back-scattering by the *whole Al crystal*.

In advance of section 7 it can be stated that for substitutional impurities, e.g. Cu in Al, the importance of back-scattering is less pronounced than it is for interstitial impurities. The Friedel expression, with differences of host and impurity phase shifts instead of just the impurity phase shifts, gives $\rho_0 = 0.34 \mu\Omega \text{ cm/at.}\%$. A calculation in an Al crystal with $A = \mathbf{1}$ gives $\rho_0 = 0.68 \mu\Omega \text{ cm/at.}\%$. Correctly accounting for back-scattering between the Cu impurity atom and the otherwise perfect Al lattice gives $\rho_0 = 0.93 \mu\Omega \text{ cm/at.}\%$.

5. Results for interstitials in bcc metals

Only the tetrahedral site (point group D_{2d}) will be considered, for this is known to be the equilibrium position for hydrogen atoms in V, Nb and Ta [2, 35]. Although larger atoms like C and O are presumably located at the octahedral site (D_{4h}) they will also be placed at the tetrahedral site in the present work, in order to get an impression of ρ_0 . A first shell of four equivalent atoms surrounds the tetrahedral site.

Owing to the lower symmetry of these systems when compared to impurities in FCC metals, the required computer time for the evaluation of the Fermi surface integrals in equation (14) increased significantly. Whereas for an octahedral impurity in an FCC metal the integrations could be restricted to the irreducible 1/48th part of the Fermi surface, in BCC systems the integrations had to be extended to 6/48th part.

An interstitial at a specific tetrahedral site results in a diagonal 3×3 resistivity tensor with, for instance, $(\rho_0)_{xx} \neq (\rho_0)_{yy} = (\rho_0)_{zz}$. Each host atom in the BCC lattice is surrounded by a collection of 24 tetrahedral sites reflecting the cubic symmetry of the host metal. Averaging over all possible impurity orientations, i.e. over these 24 sites, results in $\rho_0 = \frac{1}{3} \text{tr} \rho_0$.

All experimental data for H in V [36–39], Nb [37–39] and Ta [37, 39, 40] have been obtained at definitely non-zero temperatures. The resistivity due to hydrogen turned out to depend only very weakly on temperature in the range 390 to 940 K [39]. So, if one

Table 4. Residual resistivities in $\mu\Omega$ cm/at. % for interstitial H, C and O at the tetrahedral site in BCC metals. Column 2 shows calculated values for a single interstitial in a perfect host. Columns 3 to 8 display calculated ρ_0 values as a function of the lattice deformation of the first shell. The last two columns show available experimental information.

System	ρ_0							Experimental	
	Imp. only	0%	1%	2%	3%	4%	5%	$\Delta\rho$	Δ (%)
V(H)	0.26	0.37	0.47	0.74	1.11	1.57	2.11	0.85–1.12	4.3
Nb(H)	0.22	0.34	0.46	0.72	1.07	1.52	2.08	0.63–0.69	3.0
Nb(C)	2.58					3.51			
Nb(O)	3.36					3.69			
Ta(H)	0.13	0.16	0.29	0.55	0.94	1.47	2.09	0.71–0.92	2.5

compares calculated ρ_0 values with experimental resistivity changes $\Delta\rho$, the validity of Mathiessen's rule is implicitly assumed. The experimental lattice distortions in table 4 have been taken from a paper by Behr *et al* [41].

5.1. V(H), Nb(H) and Ta(H)

The single hydrogen in a perfect vanadium lattice causes an already considerable resistivity (see table 4). When the first shell is accounted for in the calculation, a marked dependence on lattice distortion is observed. The range of experimental $\Delta\rho$ values falls between 2% and 3% lattice distortion, which is more than 1% lower than the experimental value of 4.2%.

Both in V(H) and in Nb(H) inclusion of the first shell with 3% lattice distortion enhances the resistivity by a factor of about 4.5. In Nb the experimental $\Delta\rho$ values are reproduced at about 2% lattice distortion, which again is 1% below the experimental value of 3%. It is noted that the residual resistivity of hydrogen in V and Nb behaves almost the same as a function of lattice deformation, although the lattice constants of the two metals are different (see table 4). This means that it can be considered as justified to conclude that the experimentally found difference in $\Delta\rho$ is a consequence of a different lattice deformation around the hydrogen atom.

For Ta(H) the situation is different. Here the hydrogen atom alone leads to a residual resistivity that is approximately half of that in V and Nb. Addition of the first shell and accounting for 2% to 3% lattice distortion and for charge transfer from the hydrogen atom to the surrounding atoms results in ρ_0 values that compare well with the experimental $\Delta\rho$ range for Ta(H) in table 4. This local deformation of the lattice is in agreement with the experimental value of Behr *et al* [41]. At higher percentages lattice distortion ρ_0 approaches the values found in V and Nb. This illustrates the large influence of local lattice distortion in these BCC metal/hydrogen systems. The contribution to ρ_0 from the hydrogen and the accompanying charge transfer to its surroundings is overshadowed by the increase in cross section due to the lattice distortion caused by the proton.

In addition the residual resistivity of tetrahedral C and O in Nb was calculated. No experimental data are available. From table 4 it is seen that these impurities alone give a considerable change in resistivity when compared with H. If the first shell is included (3.5% lattice distortion) the ρ_0 values increase by a factor of 1.4 and 1.1 for C and O

respectively. This contrasts with the much larger factor of approximately 5 for hydrogen. Carbon and oxygen behave more or less like a real single-site point defect while the effect of interstitial hydrogen on the electronic structure of Nb largely proceeds via the first shell.

6. Hydrogen/deuterium isotope effect

The absence of a significant isotope effect in ρ_0 for hydrogen in Pd [32, 39] and in $\Delta\rho$ in V, Nb and Ta [37, 39] is firmly established by experiment but is not self-evident [39]. Dingle temperatures and relative cross-sectional area changes, the so-called de Haas-van Alphen scattering quantities, do depend on the kind of hydrogen isotope in Pd [42–44]. This isotope effect is large only for the two extremal orbits on the small ellipsoidal hole pockets around the point X in k -space. These X-hole pockets contribute less than 5% to the total Fermi surface area. This is also reflected in the contributions to the conductivity in the dilute system. In Pd(H), at 1% lattice distortion, the total conductivity σ is given by the sum of $\sigma_\Gamma = 0.88$, $\sigma_{JG} = 0.90$ and $\sigma_X = 0.14 \mu\Omega^{-1} \text{ cm}^{-1} \text{ at.}\%$ for the Γ sheet, the jungle gym (JG) and the X-hole pockets respectively. So possible isotope effects in σ_X are not expressed very strongly in the final value for ρ_0 . Now, realizing that the difference in the induced lattice distortion vanishes or at least is very small for the two isotopes [30], the situation in Pd becomes clear. The hydrogen isotope, which by itself is an extremely weak scatterer, introduces a lattice distortion of 1% (both for H and D) giving rise to the measured ρ_0 value. Differences in ρ_0 due to a difference in the zero-point motion (ZPM) for the isotopes are of the same order of magnitude as the resistivity due to the hydrogen alone (i.e. $\sim 0.001 \mu\Omega \text{ cm/at.}\%$), which is beyond the usual experimental accuracy. A reduced conductivity σ_X by a factor of 2, due to a possible resonant vibration in the Pd(D) cluster as proposed by Oppeneer *et al* [45], would not really change the conclusion concerning the sample resistivity.

In V, Nb and Ta the situation is slightly different, for the hydrogen isotope alone gives rise to an appreciable residual resistivity when compared with the calculation including the perturbed first shell (see table 4). In order to investigate possible ZPM effects the residual resistivity was recalculated but now with the impurity slightly displaced from its equilibrium position in the [100] direction. Such displacements can be accounted for [17] in using the appropriate interstitial displacement vector Δ_I in equation (10). No difference in the lattice expansion due to H and D in Nb could be observed [30]. A 3% lattice distortion allows for a maximum value $\Delta_I = 0.076a$, thereby still avoiding overlapping spheres. Calculated ρ_0 values did vary from $1.07 \mu\Omega \text{ cm/at.}\%$ at $\Delta_I = 0$ to $1.02 \mu\Omega \text{ cm/at.}\%$ at $\Delta_I = 0.05a$. From this no large ZPM effects are to be expected, which confirms the experimental observations.

7. Substitutional impurities

In BCC metals as well as in FCC metals an impurity cluster, consisting of a solute metal atom and its symmetrically perturbed surroundings, exhibits cubic point-group symmetry. This high symmetry is destroyed in considering an impurity–vacancy pair. However, averaging over all orientations of the pair ensures that an isotropic residual resistivity is obtained in cubic host metals.

Table 5. Residual resistivities in $\mu\Omega$ cm/at. % for dilute substitutional alloys in FCC and BCC metals. Column 2 shows calculated values for the single impurity in a perfect host. Columns 3 to 6 display calculated ρ_0 values as a function of the lattice deformation of the first shell. The last column shows available experimental information.

System	ρ_0					Experimental
	Imp. only	-0.5%	0%	+0.5%	1%	
Cu(Cu)	0.0	0.004	0.0	0.003	0.013	
Cu(Ag)	0.189	0.150	0.140	0.140	0.151	0.14
Cu(Rh d^8s^1)	0.636	1.006	0.947	0.907	0.884	4.03 ± 0.06
Cu(Rh d^9s^0)	15.7	14.6	14.1	13.6	13.1	
Cu(Rh scp)	2.99		2.98			
Cu(vac)	0.864	1.00	0.964	0.939		0.85 ± 0.21
Cu(Ag, vac)	0.977					
Ag(Ag)	0.0	0.004	0.0	0.004	0.015	
Ag(Sb)	4.88	5.43	5.51	5.60	5.69	6.2 ± 0.2
Ag(vac)	0.834	0.994	0.960	0.938		
Ag(Sb, vac)	6.52					
Al(Al)	0.0	0.003	0.0	0.003	0.011	
Al(Cu)	0.932	0.840	0.833	0.830		0.80 ± 0.06
Al(V)	2.06	4.50	4.49	4.48		7.6 ± 0.2
Al(Ni)	1.64	1.68	1.66	1.64		2.9 ± 0.3
Al(vac)	0.926	0.936	0.954	0.974		
Al(Cu, vac)	1.85					
Pd(Pd)	0.0	0.047	0.0	0.042	0.162	
Pd(Ag)	0.519	0.550	0.532	0.597	0.746	1.23
Nb(Nb)	0.0	0.042	0.0	0.040	0.158	
Nb(Ta d^3s^2)	0.044	0.098	0.035	0.054		0.23
Nb(Ta d^4s^1)	0.522	0.569	0.413	0.348		
Nb(Cr)	0.400	0.434	0.429	0.511	0.683	
Nb(Fe)	5.94	6.36	6.50	6.66		
Nb(vac)	5.70	6.48	6.50	6.57		
Nb(Ta d^3s^2 , vac)	5.80					
Nb(Ta d^4s^1 , vac)	6.25					
Nb(Cr, vac)	6.15					
Nb(Fe, vac)	8.33					

Table 5 displays calculated ρ_0 values. For the systems, given in the first column, both single-site and impurity cluster calculations have been performed. In a first calculation only the impurity, without any environmental effects, was taken into account (column 2). No constant energy shift has been applied to the impurity potential, so the Friedel sum criterion was generally not met. The first shell of 12 (FCC systems) or eight (BCC systems) perturbed host atoms was accounted for in the second type of calculation. The columns 3 to 6 show the variation of ρ_0 as a function of lattice distortion, which was varied between $-0.005a$ and $0.01a$ for the radial inward or outward displacement of the first shell atoms. In these calculations the potentials were made to fulfil the Friedel sum rule by application of a single constant energy shift to all MT potentials in the embedded cluster. The last column gives experimental data, if available.

7.1. FCC metals

In Cu, Ag, Al and Pd a host MT radius of $0.325a$ was used, which corresponds to non-touching spheres, ensuring that a slight displacement of first-shell atoms can be accounted for. For the first time the effect on ρ_0 of a perturbed first shell, including lattice distortion, could be investigated without approximating the real host embedding and beyond the applicability range of a model (pseudo)potential description of the host.

Mertig *et al* [7] calculated the residual resistivity of many impurities in Cu using self-consistently determined impurity potentials [9]. In these calculations one single perturbed site was accounted for in an otherwise perfect host. From a comparison of finite cluster results and these single-site results including the Cu band structure with experimental data [1], it was found that for Cu(Ag) the calculated ρ_0 values are structurally too low. It is seen that the residual resistivity for Cu(Ag) in table 5, using constructed potentials, is in surprisingly good agreement with experiment. Note that lattice distortion affects the results only slightly, which also is reflected in the artificial Cu(Cu) system.

In Cu(Rh) Julianus *et al* [46] accurately measured ρ_0 . Constructed potentials with Rh in its experimental atomic ground state ($[\text{Kr}]4d^85s^1$) result in values far too low, while the $[\text{Kr}]4d^95s^0$ configuration for Rh leads to values that are much larger than the experimental value of $4.03 \pm 0.06 \mu\Omega \text{ cm/at. \%}$. Presumably the electronic structure of Rh in Cu is intermediate between $[\text{Kr}]4d^85s^1$ and $[\text{Kr}]4d^95s^0$. This is in accordance with the ρ_0 values obtained from self-consistent potentials (Cu(Rh SCP) in table 5). Although here a lattice constant $a = 6.76$ Bohr was used in combination with touching MT spheres, the results are improved significantly when compared with those obtained from constructed potentials. For a vacancy in Cu the agreement with experiment is within the experimental error, regardless of the presence of a first shell with or without lattice distortion.

One could wonder how the results are influenced upon using host MT radii corresponding to touching spheres, for local lattice distortion does not seem to be that important. In order to get an impression of the residual resistivities obtained in this way a single-site calculation was performed. The MT radius and Fermi energy are given in table 3. Resistivities of $0.12 \mu\Omega \text{ cm/at. \%}$ for Cu(Ag), $0.57 \mu\Omega \text{ cm/at. \%}$ for Cu(Rh d^8s^1), $13.8 \mu\Omega \text{ cm/at. \%}$ for Cu(Rh d^9) and $1.052 \mu\Omega \text{ cm/at. \%}$ for Cu(vac) are found. The resistivity due to a vacancy is increased and approaches the calculated value reported in [1]. All other ρ_0 values are lowered. The nice agreement with experiment in Cu(Ag) and Cu(vac) is spoiled.

In Ag(Sb) qualitative agreement with experiment is obtained. For a larger MT radius the situation is expected to get worse on the basis of former observations made in, for instance, Cu(Rh). A vacancy in Ag gives rise to a residual resistivity that is slightly lower than that in Cu. Inclusion of the first shell indeed influences ρ_0 although lattice distortion seems to be of little importance. The resistivity due to a Sb-vacancy pair is larger than the sum of the resistivities caused by the individual defects, though the difference is not spectacular.

In pure Al again a very small residual resistivity was found upon deforming the lattice. For Al(Cu) the agreement is within 17% in the single-site case. The calculated value of ρ_0 equals the experimental value after adding the first shell, as was found before in Cu(Ag). In the dilute V and Ni alloys of Al the agreement between theory and experiment is less satisfactory. The experimental data on Al alloys in table 5 were taken from [47]. The resistivity in Al(Cu, vac) almost equals the sum of the single-site resistivities in Al(Cu) and Al(vac), thereby neglecting environmental effects.

In Pd the Fermi level falls in the d band. This gives rise to a complicated electronic structure at the Fermi energy, contrary to the situation in Cu and Ag, where the d band is well below ε_F . In Al no d electrons are present at all. The sensitivity to lattice deformation is found to be a factor of 10 larger in Pd(Pd) when compared with Cu, Ag and Al. This cannot be explained simply from the density of states at the Fermi energy for this effect would point in the opposite direction. A plausible explanation is offered in realizing that d electrons behave rather localized (flat ε_{nk} versus k relation) in contrast with s electrons (parabolic shape of ε_{nk} versus k relation). When a transition-metal atom (Pd, Cu or Ag) is displaced from its equilibrium position it will drag its d electrons along, giving rise to an appreciable alteration in the spatial charge distribution. In Pd the d electrons at ε_F , in Bloch states with only little dispersion, carry the electric current. These d electrons are strongly scattered by the perturbation potential resulting from the lattice deformation which in turn is expressed as a substantial resistivity increase. Truly delocalized s electrons at ε_F in Cu and Ag are not that sensitive to the precise position of the host metal nuclei, indicating that for these metals a jellium-like description of the electrons at ε_F might lead to satisfactory results.

For Pd(Ag) the agreement with experiment is not very satisfactory, although the situation is not as bad as in non-self-consistent Cu(Rh). At 1% lattice distortion the calculated residual resistivity is only about half of the experimental value, probably due to the complicated electronic structure of the palladium host and of the impurity cluster.

7.2. Nb, a BCC metal

Up to the present no calculated residual resistivities in BCC transition metals have been reported on. Presumably the limited number of systems for which ρ_0 has been determined experimentally is a drawback. However, considerable interest exists in the scattering properties of substitutional impurities in Nb in connection with electromigration theory [14, 48, 49]. In this section several impurities in Nb will receive attention as well as vacancy-impurity pairs. An elementary step in the diffusion (and thus in electromigration) of substitutional impurities in Nb is thought to proceed via a mechanism whereby the impurity exchanges position with a neighbouring vacancy.

In close analogy to the FCC systems treated in section 7.1 a host MT radius smaller than that corresponding to touching spheres ($R_{MT}^{\text{host}} = 0.433a$) was used. Again the same MT radius ($0.335a$) as for the interstitial-impurity study was used. Note however that in BCC metals the reduction of this radius compared with the radius corresponding to touching spheres is larger than in FCC systems.

A marked dependence on lattice distortion in Nb(Nb) is found. The same explanation as for Pd(Pd) applies. For Nb also the Fermi level crosses the flat d bands. Interestingly the resistivity increase due to Ta at 0.5% lattice distortion is comparable to ρ_0 in Nb(Nb) at 0.5% lattice distortion. A vacancy in Nb, which corresponds to a $4d^45s^1$ valence electron deficiency, gives $\rho_0 = 6.50 \mu\Omega \text{ cm/at. } \%$ at 0% lattice distortion. The vacancy alone results in a lower value ($5.70 \mu\Omega \text{ cm/at. } \%$). These large residual resistivities arise from the removal of four localized d electrons around the Fermi energy. The residual resistivity of the Ta-vacancy pair, neglecting environmental effects, is dominated by the vacancy. This also holds for the Cr-vacancy pair. Replacement of a Nb atom by an Fe atom with an $[\text{Ar}]3d^65s^2$ configuration also leads to a considerable resistivity, comparable to that due to a vacancy. It is therefore not surprising to find the Fe-vacancy pair giving the largest residual resistivity in Nb of all defects investigated here. Possible magnetic moments on Cr or on Fe have been neglected.

Using a larger host MT sphere of $0.391a$ (see table 3) resulted in lower residual resistivities in Nb(vac). Neglecting the first shell a value $\rho_0 = 4.53 \mu\Omega \text{ cm/at.}\%$ is calculated, which is lower than the value of $5.70 \mu\Omega \text{ cm/at.}\%$ in the second column of table 5. Further it is noted that the experimental ρ_0 value for the Nb(Ta) system is best reproduced when using the $[\text{Xe}]4f^{14}5d^46s^1$ atomic configuration for the Ta atom. This is the analogue of the Nb $[\text{Kr}]4d^45s^1$ atomic configuration as used in the construction of the host potential. The alternative $[\text{Xe}]4f^{14}5d^36s^2$ configuration, which is the ground-state configuration in atomic Ta, resulted in much lower residual resistivities. Such a marked dependence of ρ_0 on the specific electronic configuration of the atom used in the impurity potential construction, as found for Ta in Nb or Rh in Cu, has been reported on earlier by Mrosan and Lehmann [50]. In using a larger host MT radius ($0.391a$) the residual resistivity due in Nb(Ta d^4s^1) was lowered slightly from $0.413 \mu\Omega \text{ cm/at.}\%$ to $0.364 \mu\Omega \text{ cm/at.}\%$ while for Nb(Ta d^3s^2) a relatively large change from $0.035 \mu\Omega \text{ cm/at.}\%$ to $0.016 \mu\Omega \text{ cm/at.}\%$ is observed. In these calculations lattice deformation was absent while the Friedel sum rule was satisfied.

8. Conclusions

Residual resistivities for interstitial and substitutional impurities in both FCC and BCC metals have been calculated. The KKR Green function method was used to calculate the scattering t -matrix for an impurity cluster, which was modelled by a collection of spherically symmetric muffin-tin potentials. This cluster was embedded in an otherwise perfect crystal, also modelled by a lattice of MT potentials. The influence of the perturbed metal atoms surrounding the impurity on ρ_0 was investigated thoroughly for the first time. Local charge neutrality in the impurity cluster was guaranteed by requiring fulfilment of the Friedel sum rule.

The influence of local lattice distortion around interstitial as well as substitutional impurities is pronounced in metals where the Fermi energy falls in the d band of the DOS (Ni, Pd, V, Nb and Ta). Other metals having an s like (Cu and Ag) or sp like (Al) DOS at ε_F do not show a large dependence of ρ_0 on the lattice distortion. This is explained through the localized character of the d electrons when compared with the s and p electrons. A slight displacement of a transition-metal atom will drag the d electrons along with it, giving rise to a relatively large local change in charge density. The d electrons in Bloch states at ε_F with a flat dispersion relation are strongly scattered by the resulting potential. Electrons in delocalized s -like Bloch states do not follow the metal atoms that strictly, resulting in a much smaller resistivity increase as a function of lattice deformation.

It was found that, on the one hand, hydrogen *alone* in Cu and Ag constitutes a strong scatterer contributing about 90% of the total resistivity. On the other hand, in Pd and Ni it does not result in a significant residual resistivity. Hydrogen without a first shell in V, Nb and Ta gives ρ_0 values intermediate between the above-mentioned extremes. Except for H in Cu and Ag, the inclusion of the first shell is an absolute necessity in order to obtain values comparable with measured data. Hydrogen/deuterium isotope effects on the basis of a difference in zero-point motion are not to be expected in Pd, V, Nb and Ta, which is in agreement with experiment.

Huge contributions due to the back-scattering by the Al crystal were detected in Al(H). This explains the large difference between, on the one hand, results obtained from the Friedel expression or from finite cluster calculations and, on the other hand,

residual resistivities obtained in the real Al lattice. Such strong effects were not found in Cu(H), Ag(H) and the substitutional Al alloys.

An ever returning point of discussion is the choice of the MT radii for the host and interstitial atoms. One might argue that for each system there exists an optimum ratio R_{MT}^{host}/R_{MT}^I at which experiment and theory match. Such a ratio indeed can be found for the Cu(H) system but for Pd(H), at the experimental lattice distortion ($\sim 1\%$), the existence of such a ratio in the present MT model is highly questionable. Therefore a more uniform approach was selected. For interstitial impurities in FCC metals the prescription of Switendick [51] was followed ($R_{MT}^{host}/R_{MT}^I = 1.86$). For interstitials in BCC metals a different ratio of 1.5 was used. All MT radii obtained in this manner have in common that the interstitial MT radius lies between 1.20 and 1.40 Bohr. In this way the interstitial MT spheres do justice to the maximum in the radial charge distribution of the hydrogen atom in its ground state. Such a maximum corresponds to a more or less localized state, which has been found in several metal-hydrogen systems [52, 53].

Touching host MT spheres always have the disadvantage that they do not allow for lattice deformation. In many systems lattice deformation is present around the defect and it can influence the residual resistivity considerably. The R_{MT}^{host}/R_{MT}^I ratios used throughout this paper make it possible to account for these effects.

In the substitutional FCC metal-impurity systems investigated in this work the description using a MT radius of $0.325a$ led to good results in Cu(Ag), Cu(vac) and Al(Cu). For Ag(Sb), Al(V) and Al(Ni) qualitative agreement is obtained while non-self-consistent Rh in Cu is problematic. Lattice distortion is only important in Pd having a large d-like DOS at ε_F . In most cases the inclusion of a first shell of perturbed host atoms did improve the ρ_0 values, but not to such an extent that discrepancies between theory and experiment disappeared. Increase of the host MT radius to $0.354a$ (touching spheres) leads to less satisfactory values for ρ_0 . Touching spheres might overestimate the part of the crystal potential that can be approximated safely by a spherically averaged potential, but the precise cause is not clear.

In the BCC metal Nb the substitution of a vacancy or an Fe atom gives a large residual resistivity while for Ta or Cr, roughly speaking, ρ_0 is a factor of 10 smaller. In a sense this reflects the differences in the number of valence electrons (ΔZ) which are -5 , $+3$, 0 and $+1$ for a vacancy, Fe, Ta and Cr respectively. The influence of lattice distortion in Nb can be considerable (Nb(Ta)).

It is found that the residual resistivity due to an impurity-vacancy pair can be estimated by summing the single-site values for ρ_0 of the individual scatterers. However, if both the impurity and the vacancy are strong scatterers, multiple scattering effects can be large. In Nb(Fe, vac) a reduction was found amounting to 30%.

Fulfilment of the Friedel sum rule in substitutional alloys was obtained by shifting all MT potentials in the impurity cluster by the same constant potential. This choice is expected to give reliable results in those cases where charge transfer to or from the first shell is reasonably approximated in constructing the alloy potential by overlapping atomic charge densities. In allowing for different shifts for the impurity and the first shell one introduces a degree of freedom. This degree of freedom could then be used to simulate large flows of charge in the impurity cluster. Test calculations showed that the results for Cu(Rh) can be improved in this way starting from either of the two Rh configurations. In the present work such manipulations were avoided. Precise information on these charge flows should come from a self-consistent approach. The potentials constructed from atomic charge densities in combination with a single constant energy shift for all perturbed transition-metal atoms clearly give good results in situations

where the defect has a relatively simple electronic structure. Interstitial hydrogen is an example of such a defect as well as the substitutional systems Cu(Ag) and Al(Cu). In cases where impurity d electrons are to be redistributed in virtual bound states around the Fermi energy, calculated residual resistivities show larger deviations from the experimental data. Nevertheless in some cases reasonable results can be obtained (e.g. Nb(Ta)).

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