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Calculation of the Residual Resistivity and the Thermoelectric Power of sp Impurities in Silver

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We present *ab initio* calculations for the residual resistivity and the thermopower of *sp* impurities in silver. The calculations are based on density-functional theory and the Korringa-Kohn-Rostoker Green's-function method. The linearized Boltzmann equation is solved by means of a Fermi-surface harmonic expansion to calculate the residual resistivity, taking into account the anisotropic electronic properties of the dilute alloy. The thermoelectric power was obtained from the energy dependence of the residual resistivity by means of Mott's formula. The results are in satisfying agreement with highly precise experimental results and confirm experimentally obtained deviations from a quadratic dependence on the valence difference ΔZ for the thermopower of *sp* impurities in silver.

I. INTRODUCTION

Green's-function methods[1] offer a convenient and elegant way to solve the inhomogeneous problem of a single impurity in an otherwise ideal crystal. The aim of this paper is the calculation of transport coefficients of dilute alloys on an *ab initio* basis using density-functional theory. The calculations apply the Korringa-Kohn-Rostoker (KKR) Green's-function method[1] in the case of a strongly localized impurity in an otherwise ideal host crystal. That is, the potential perturbation is restricted to one cell only and lattice relaxations around the impurity are neglected.

For the calculation of the transport coefficients, like residual resistivity and thermopower, the Boltzmann equation is solved by means of expansion in terms of Fermi-surface harmonics (FSH) (Refs. 2–4) taking into consideration the anisotropic electronic properties of the dilute alloy.

Highly precise experimental results for the residual resistivity and thermoelectric power of *sp* impurities in silver show, in difference to analogous results in copper, deviations from the expected quadratic dependence on the valence difference ΔZ.[5] The aim of this paper is this problem within a first-principles treatment.

This paper is organized as follows. In Sec. II we present the theoretical background for the calculation of the residual resistivity and thermoelectric power. The numerical details of the calculation are given in Sec. III, and a discussion of the calculated values in comparison to experimental results is presented in Sec. IV.

II. THEORY

A. Boltzmann equation

The residual resistivity of the impurities is calculated by solving the linearized Boltzmann equation

$$e \frac{\partial f_k^0}{\partial \epsilon_k} \mathbf{v}_k \cdot \mathbf{E} = \sum_{k'} P_{kk'} \left(f_{k'} - f_k \right) \tag{1}$$

for the electron distribution function $f_k = f_k^0 + g_k$ under the influence of a homogeneous electric field $\mathbf{E}$. Here f_k^0 is the Fermi-Dirac equilibrium distribution function and $P_{kk'}$ is the transition probability due to electron-impurity scattering. Writing the deviation of the electron distribution g_k in linear response to the external electric field $\mathbf{E}$,

$$g_k = e\delta(\epsilon_k - \epsilon_F)\mathbf{\Lambda}_k \cdot \mathbf{E}, \tag{2}$$

a linear integral equation for the vector mean free path $\mathbf{\Lambda}_k$,

$$\mathbf{\Lambda}_k = \tau_k \left(\mathbf{v}_k + \sum_{k'} P_{kk'} \mathbf{\Lambda}_{k'} \right), \tag{3}$$

has to be solved. The relaxation time τ_k is defined by

$$\tau_k^{-1} = \sum_{k'} P_{kk'}. \tag{4}$$

With the solution of (3) the electric current becomes

$$\mathbf{j} = 2\frac{e^2}{V} \sum_k \delta(\epsilon_k - \epsilon_F)\mathbf{v}_k \left(\mathbf{\Lambda}_k \cdot \mathbf{E} \right). \tag{5}$$

In comparison to Ohm's law one gets the conductivity tensor

$$\overset{\leftrightarrow}{\sigma} = 2\frac{e^2}{V} \sum_k \delta(\epsilon_k - \epsilon_F)\mathbf{v}_k \mathbf{\Lambda}_k \tag{6}$$

and the residual resistivity tensor $\overset{\leftrightarrow}{\rho}$ by inversion of $\overset{\leftrightarrow}{\sigma}$.

B. Application of the Fermi-surface harmonics to the Boltzmann equation

A way to solve the Boltzmann equation is to expand the vector mean free path $\Lambda_{\mathbf{k}}$ in sets of Fermi-surface harmonics (FSH). The FSH consist of all polynomials of the Cartesian components of the electron velocity $\mathbf{v_k}$ orthonormalized on the real Fermi surface.[2] That is, for each integer $N \geq 0$ we construct all polynomials of $(v_x)^l (v_y)^m (v_z)^n$ with $l, m, n \geq 0$ and $l + m + n = N$ and orthonormalize them on the anisotropic Fermi surface according to

$$\frac{\sum_{\mathbf{k}} \delta(\epsilon_{\mathbf{k}} - \epsilon_F) \Psi_M(\mathbf{k}) \Psi_{M'}(\mathbf{k})}{\sum_{\mathbf{k}} \delta(\epsilon_{\mathbf{k}} - \epsilon_F)} = \delta_{MM'} \qquad (7)$$

(M is a convenient label of the FSH). Hence, $\Lambda_{\mathbf{k}}$ is expanded in terms of FSH,

$$\Lambda_{\mathbf{k}} = \sum_M \Lambda_M \Psi_M(\mathbf{k}) . \qquad (8)$$

Combining (3) and (8), and using the orthogonality relation (7), the Boltzmann equation can be transformed into the resulting algebraic set[2,4]

$$\sum_M (\delta_{MM'} - C_{MM'}) \Lambda_{M'} = \mathbf{D}_M \qquad (9)$$

with the matrix

$$C_{MM'} = \frac{\sum_{\mathbf{k}} \sum_{\mathbf{k}'} \delta(\epsilon_{\mathbf{k}} - \epsilon_F) \tau_{\mathbf{k}} \Psi_M(\mathbf{k}) P_{\mathbf{kk}'} \Psi_{M'}(\mathbf{k}')}{\sum_{\mathbf{k}} \delta(\epsilon_{\mathbf{k}} - \epsilon_F)} \qquad (10)$$

and the vector

$$\mathbf{D}_M = \frac{\sum_{\mathbf{k}} \delta(\epsilon_{\mathbf{k}} - \epsilon_F) \tau_{\mathbf{k}} \Psi_M(\mathbf{k}) \mathbf{v_k}}{\sum_{\mathbf{k}} \delta(\epsilon_{\mathbf{k}} - \epsilon_F)} . \qquad (11)$$

Equation (9) may be solved approximately by truncating the polynomial expansion at a finite order N. In this way the solution of the integral equation (3) is reduced to a solution of the algebraic set (9) for the coefficients Λ_M.

C. The transition probabilities

For elastic scattering the transition probability $P_{\mathbf{kk}'}$ is given by

$$P_{\mathbf{kk}'} = cN \frac{2\pi}{\hbar} \mid T_{\mathbf{kk}'} \mid^2 \delta(\epsilon_{\mathbf{k}} - \epsilon_F), \qquad (12)$$

where $T_{\mathbf{kk}'}$ is the T matrix for impurity scattering. N is the number of atoms in the crystal and c is the concentration of impurity atoms. In the case of cubic symmetry and limitation of angular momenta to $l \leq 2$ the T matrix for a single scattering potential in an otherwise ideal host

is given by

$$T_{\mathbf{kk}'} = -\left[\frac{\hbar^2}{2m}\right]^{\frac{3}{2}} \epsilon_F^{-\frac{1}{2}} \sum_L c_L(\mathbf{k}) c_L(\mathbf{k}') I_L \qquad (13)$$

with

$$I_L = \frac{\sin \Phi_L(E) \exp \Phi_L(E)}{\operatorname{Im} A_{LL}(E)}. \qquad (14)$$

The quantities c_L are the coefficients of the Bloch waves in an angular momentum expansion. L represents a shorthand notation for the irreducible representations l_α, that is, Γ_1 for $l = 0$, Γ_{15} for $l = 1$, $\Gamma_{12}, \Gamma_{25'}$ for $l = 2$, and the number of basic functions m_α belonging to an irreducible representation. A_{LL} are the expansion coefficients of the host Green function. $\Phi_L(E)$ are the effective phase shifts defined by

$$\tan \Phi_L = \operatorname{Im} A_{LL} \tan \Delta\eta_l / (1 - \operatorname{Re} A_{LL} \tan \Delta\eta_l) \qquad (15)$$

with the difference $\Delta\eta_l$ between the scattering phase shifts of an impurity atom and a host atom. For further details see, for example, Mertig, Mrosan, and Ziesche.[6]

D. Thermoelectric power

The impurity contribution to the thermoelectric power S_{imp} can be calculated by means of Mott's formula,[7,8]

$$S_{\text{imp}} = \frac{\pi^2 k_B^2 T}{3 \mid e \mid} \left[\frac{\partial \ln \rho}{\partial \epsilon}\right]_{\epsilon = \epsilon_F}, \qquad (16)$$

where ρ is the residual resistivity. According to (16) the knowledge of the energy dependence of the host and impurity properties is necessary to calculate the thermoelectric power S_{imp}. To determine the energy derivatives in (16), the integrations have to be performed over the Fermi surface and also over surfaces of constant energy near E_F. The numerical details are described in the following section.

III. TECHNICAL DETAILS OF THE CALCULATION

The calculations are performed within the frame of density-functional theory[9,10] using the local-density approximation of Hedin and Lundqvist.[11] The band structure of the silver host was generated from the self-consistent potential given by Moruzzi, Janak, and Williams.[12] The imaginary part of the host Green's function was generated by means of a Brillouin-zone integration using the tetrahedron method.[13] The real part of the Green's function was calculated by a Kramers-Kronig integration (cutoff energy of 1.9 Ry).

With the ideal host Green's function determined in this way the effective scattering phase shifts for Zn, Ga, Ge, As and Cd, In, Sn, Sb (see Table I) were calculated self-consistently as described by Podloucky, Zeller, and Dederichs.[1]

For residual-resistivity calculations the Boltzmann equation was solved using a FSH expansion up to the

TABLE I. Effective scattering phase shifts at $\epsilon_F - 2h$, $\epsilon_F - h$, ϵ_F, $\epsilon_F + h$, $\epsilon_F + 2h$ with $h = 1$ mRy ($\epsilon_F = 0.481429$ Ry).

Impurity system	Energy	Φ_{Γ_1}	$\Phi_{\Gamma_{15}}$	$\Phi_{\Gamma_{25'}}$	$\Phi_{\Gamma_{12}}$
Ag(Zn)	$\epsilon_F - 2h$	0.382745	0.192179	0.087500	0.087363
	$\epsilon_F - h$	0.382453	0.192373	0.087610	0.087526
	ϵ_F	0.382052	0.192302	0.087800	0.087800
	$\epsilon_F + h$	0.381748	0.192411	0.087896	0.087946
	$\epsilon_F + 2h$	0.381380	0.192442	0.088007	0.088111
Ag(Ga)	$\epsilon_F - 2h$	0.811457	0.503586	0.115905	0.114863
	$\epsilon_F - h$	0.810654	0.503296	0.116109	0.115128
	ϵ_F	0.809691	0.502452	0.116419	0.115538
	$\epsilon_F + h$	0.808879	0.502123	0.116605	0.115780
	$\epsilon_F + 2h$	0.807836	0.501456	0.116813	0.116050
Ag(Ge)	$\epsilon_F - 2h$	1.196800	0.876818	0.131670	0.129939
	$\epsilon_F - h$	1.195882	0.875178	0.131950	0.130280
	ϵ_F	1.194845	0.872995	0.132349	0.130785
	$\epsilon_F + h$	1.193931	0.871640	0.132609	0.131099
	$\epsilon_F + 2h$	1.192641	0.869553	0.132894	0.131448
Ag(As)	$\epsilon_F - 2h$	1.514536	1.268328	0.141357	0.139138
	$\epsilon_F - h$	1.513816	1.265162	0.141689	0.139530
	ϵ_F	1.513061	1.261858	0.142150	0.140098
	$\epsilon_F + h$	1.512359	1.259436	0.142462	0.140463
	$\epsilon_F + 2h$	1.511229	1.255977	0.142802	0.140866
Ag(Cd)	$\epsilon_F - 2h$	0.283667	0.211589	0.066034	0.066286
	$\epsilon_F - h$	0.283227	0.211624	0.066067	0.066363
	ϵ_F	0.282703	0.211371	0.066161	0.066525
	$\epsilon_F + h$	0.282255	0.211318	0.066185	0.066590
	$\epsilon_F + 2h$	0.281770	0.211175	0.066218	0.066668
Ag(In)	$\epsilon_F - 2h$	0.609002	0.535276	0.102007	0.101463
	$\epsilon_F - h$	0.608050	0.534584	0.102157	0.101670
	ϵ_F	0.606950	0.533325	0.102399	0.102007
	$\epsilon_F + h$	0.605988	0.532615	0.102534	0.102194
	$\epsilon_F + 2h$	0.604881	0.531537	0.102685	0.102405
Ag(Sn)	$\epsilon_F - 2h$	0.883873	0.879282	0.126605	0.125110
	$\epsilon_F - h$	0.882650	0.877143	0.126862	0.125428
	ϵ_F	0.881269	0.874464	0.127235	0.125905
	$\epsilon_F + h$	0.880041	0.872616	0.127472	0.126198
	$\epsilon_F + 2h$	0.878551	0.870039	0.127735	0.126523
Ag(Sb)	$\epsilon_F - 2h$	1.146484	1.247398	0.149337	0.146679
	$\epsilon_F - h$	1.145221	1.243684	0.149710	0.147110
	ϵ_F	1.143830	1.239802	0.150218	0.147727
	$\epsilon_F + h$	1.142569	1.236809	0.150568	0.148128
	$\epsilon_F + 2h$	1.140948	1.232796	0.150951	0.148572

TABLE II. Dependence of the residual resistivity of Ag(Zn) and Ag(As) on the order of expansion of FSH.

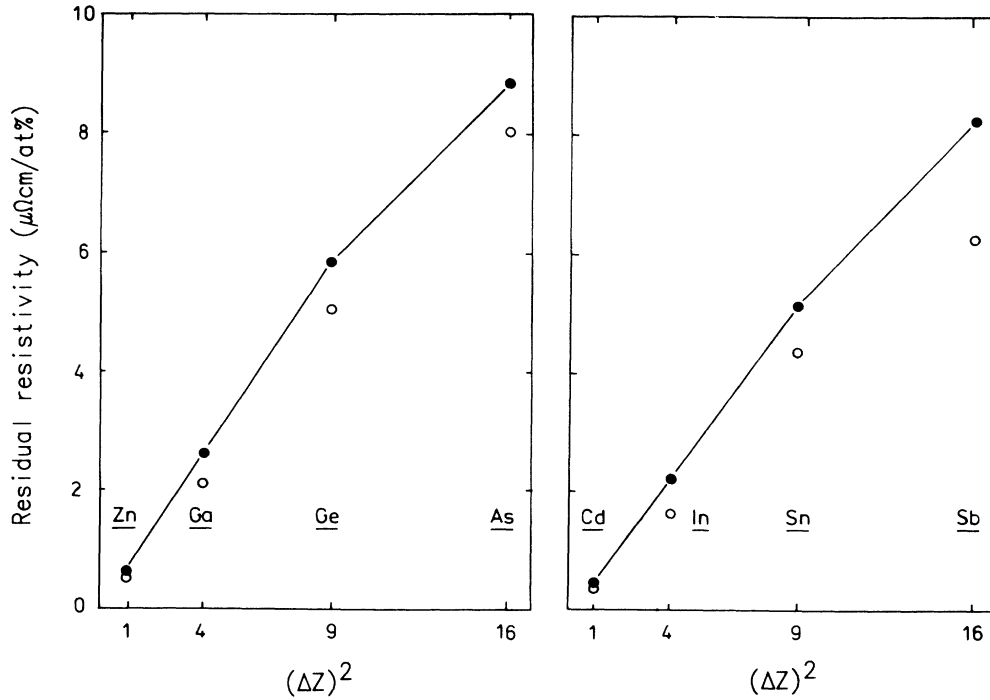| Impurity system	ρ in $\mu\Omega$ cm/at.%			
	First order	Third order	Fifth order	Seventh order
Ag(Zn)	0.55137	0.55132	0.55047	0.54990
Ag(As)	8.82914	8.75314	8.73211	8.71257

FIG. 1. Residual resistivity of dilute silver alloys: left, sp impurities of the fourth row; right, sp impurities of the fifth row of the Periodic Table. Experimental results (open circles) are taken from Ref. 15 in comparison to our calculation (closed circles).

first order of polynomials. The convergence is discussed up to the seventh order for arbitrary chosen systems (see Table II). As it was expected due to Allen,[2] the first order of polynomials is sufficient for the calculation of the residual resistivity.

To compute the energy derivative necessary to obtain the thermopower, the resistivity was calculated at energies $\epsilon_F - 2h$, $\epsilon_F - 1h$, ϵ_F, $\epsilon_F + 1h$, and $\epsilon_F + 2h$ with $h = 1$ mRy. For the derivative the following approximation was used:

$$\rho'(\epsilon_F) = \frac{1}{12h}[\rho(\epsilon_F - 2h) - 8\rho(\epsilon_F - h)$$
$$+ 8\rho(\epsilon_F + h) - \rho(\epsilon_F + 2h)]. \qquad (17)$$

The energy-surface integrations were performed by means of a modified tetrahedron method.[6] Especially in the case of silver, we found it necessary to include 6912 tetrahedra in the Fermi-surface integration.

IV. RESULTS AND DISCUSSION

A. Residual resistivity

The results for the residual resistivity of the considered sp defects in silver are shown in Fig. 1. The general agreement between theoretical and experimental results is satisfactory. The calculated residual resistivity values are generally larger than the experimental ones. This should be connected with our model of a strongly localized impurity in an otherwise perfect environment. In this model the charge difference is restricted to one per-

turbed potential only, which probably overestimates the scattering of the conduction electrons.

According to Linde's rule the residual resistivity shows a quadratic dependence on the valence difference ΔZ. For equal ΔZ we found a dependence on the atomic number, that is, the residual resistivity due to defects of the fourth row is larger than that due to defects of the fifth row, but not as large as expected from experiment.

The most important contribution to the residual resistivity stems from the scattering of p electrons. This fact becomes clear if we consider, on the one hand, the scattering phase shifts (Table I), which are large for angular momenta $l = 0$ and 1. On the other hand, the character of the wave function averaged over the Fermi surface is mainly p- or d-like,[14] which can be illustrated in terms of

$$\sum_{\mathbf{k}} \delta(\epsilon_{\mathbf{k}} - \epsilon_F) \sum_{m_\alpha} |c_{l,m_\alpha}(\mathbf{k})|^2 \qquad (18)$$

(see Table III). In combination of defect and host prop-

TABLE III. Character of the electron wave function of the ideal silver host (arbitrary units).

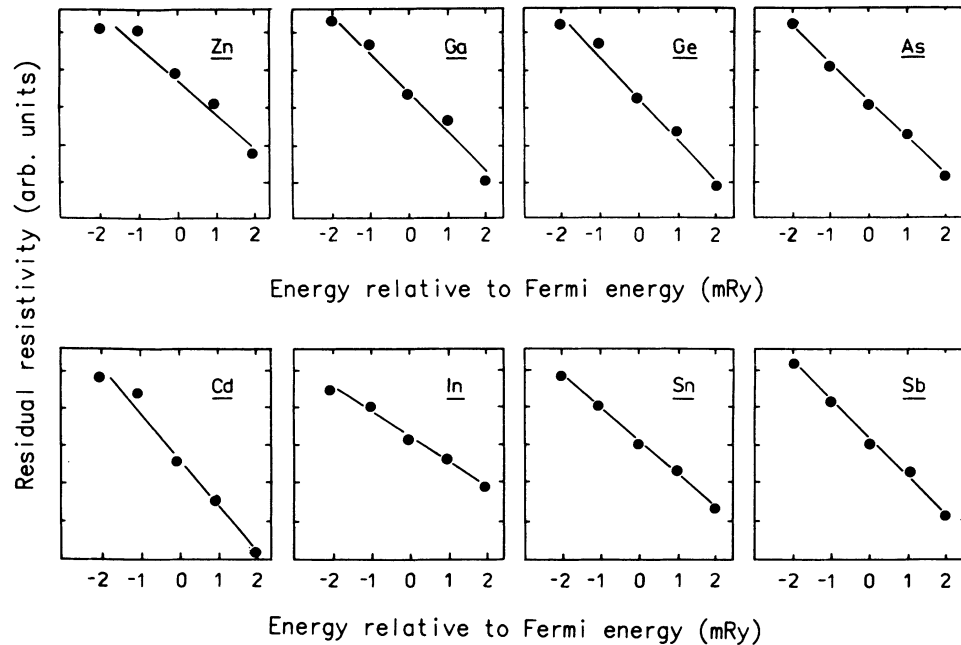| Angular momentum l	$\sum_{\mathbf{k}} \delta(\epsilon_{\mathbf{k}} - \epsilon_F) \sum_{m_\alpha} |c_{l,m_\alpha}(\mathbf{k})|^2$
s	34.775
p	165.135
d	235.768

FIG. 2.   Energy dependence of the residual resistivity of $4sp$ and $5sp$ impurities in silver.

erties the scattering of p electrons is preferred in sp silver systems. From the analysis of the $\mathbf{k}$ dependence of the relaxation time $\tau_{\mathbf{k}}$ (Ref. 14), it becomes obvious that electrons in states near the neck and belly region of the noble-metal Fermi surface are scattered strongest and consequently contribute mainly to the resistivity.

B. Thermoelectric power

The energy dependence of the residual resistivities for the sp impurities in silver is shown in Fig. 2. The general trend is a linearly decreasing energy dependence, that is, a negative thermopower for all systems under considera-
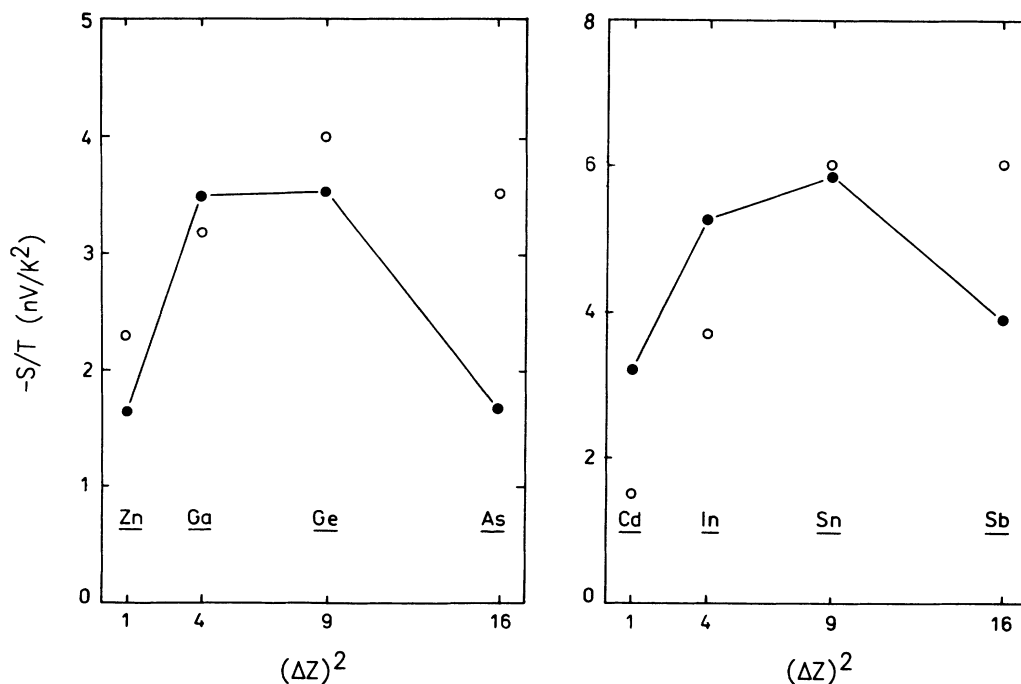
FIG. 3.   Thermoelectric power of dilute silver alloys: left, sp impurities of the fourth row; right, sp impurities of the fifth row of the Periodic Table. Experimental results (open circles), see Ref. 5 in comparison to our calculation (closed circles).

tion.

The thermopower itself is shown in Fig. 3 in comparison with results from high precession experiments of Bindke.[5] The experimental and theoretical values show a similar dependence on the valence difference ΔZ. The absolute values do not agree completely, showing that the thermopower is a very sensitive quantity. The deviations from the ΔZ^2 rule are even somewhat more strongly pronounced in the calculations than in the experiment.

The main result is that our calculation confirms the experimentally determined saturation behavior of the thermopower in dependence on the valence difference for dilute silver alloys with $\Delta Z \geq 2$.

Furthermore, the thermopower shows a pronounced dependence on the atomic number for equal ΔZ. The thermopower for sp defects of the fourth row in silver is smaller than for sp defects of the fifth row, that is, the thermopower of the lighter defects is smaller than the thermopower of heavier ones. [Note the different scales in Figs. 3(a) and 3(b).] This effect is in contrast to the behavior of the residual resistivity.

Similar to the residual resistivity, however, the most important contribution to the thermopower results from the scattering of p electrons.

V. CONCLUSIONS

The aim of this paper was to investigate the dependence on ΔZ, the valence difference between host and impurity, for the residual resistivity and the thermopower of sp impurities in silver by means of first-principles calculations. The calculated values for the residual resistivity are in good agreement with the experiment and show that Linde's rule holds for $1 \leq \Delta Z \leq 4$. The calculated thermopowers show the same dependence on ΔZ as the experimental values, that is, they differ from a quadratic dependence on ΔZ for $\Delta Z \geq 2$. To reach better quantitative agreement it seems to be necessary to include the perturbation of neighboring host atoms and lattice distortion effects around the impurity.

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