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Electronic Structure of Impurities in Dilute Alloys of Al

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Self-consistent, nonlinear screening calculations for point-ion nonmagnetic impurities in jellium are made using the Hohenberg-Kohn and Kohn-Sham density functional formalism. The Friedel criterion is used to estimate the effective impurity valency and the Blatt correction is used for the size effect. The impurity induced charge densities in the Al matrix are calculated and an analytical expression, valid in both the preasymptotic and asymptotic regions is proposed. The net impurity effective charges are calculated and it is found that the matrix makes a substantial charge transfer in the impurity cell for all the alloys except AlMg and AlSn . The estimated residual resistivities agree fairly well with available experimental data.

Selbstkonsistente, nichtlineare Abschirmrechnungen werden für nichtmagnetische Punktionen-Störstellen in Jellium mit dem Hohenberg-Kohn- und Kohn-Sham-Dichtefunktionalformalismus durchgeführt. Das Friedelsche Kriterium wird benutzt, um die effektive Störstellenvalenz zu berechnen und die Korrektur von Blatt für den Größeneffekt. Die störstelleninduzierten Ladungsdichten in der Al-Matrix werden berechnet und ein analytischer Ausdruck vorgeschlagen, der sowohl im präasymptotischen als auch im asymptotischen Bereich gültig ist. Die effektiven Nettoladungen der Störstellen werden berechnet und es wird gefunden, daß die Matrix einen wesentlichen Ladungstransfer in die Störstellenzelle für alle Legierungen außer AlMg und AlSn liefert. Die berechneten Restwiderstände stimmen ziemlich gut mit verfügbaren experimentellen Daten überein.

1. Introduction

The electronic structure of Al is usually considered on the basis of the nearly free electron model which can also be described appropriately by the pseudo-potential theory and the jellium model [1]. Indeed, the density of states of Al shows the familiar \sqrt{E} behaviour except for some anomalies caused by band gaps. Therefore, it has been tempting to describe impurities in Al as impurities in jellium. Such calculations have been performed by Mrosan and Lehmann [2] using Mattheis's prescription for the impurity potential. Lautenschläger and Mrosan [3] extended the calculations for charge transfer and Friedel oscillations. Nieminen and Puska [4] performed self-consistent jellium calculations for 3d impurities in Al in the spherical solid model of Almladh and von Barth [5]. The quality of such jellium calculations is further examined by the KKR Green's function method for magnetic and nonmagnetic impurities in Al by Deutz et al. ([6] and references therein). However, in these calculations the size effect is completely ignored and these are not used to estimate the impurity-induced charge distribution and the net charge on the impurities which are needed to explain the data for electric-field gradient, wipeout numbers, etc., and to estimate the host-impurity interaction. With this view point, a simple but realistic physical model is adopted to estimate the impurity effective charge and the nonlinear screening of the impurity by conduction electrons. The induced charge distribution around an impurity, the host-impurity potential, the charge transfer, and residual resistivities are studied.

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The plan of the paper is as follows: The physical model is presented in Section 2, the calculations and results are presented in Section 3, and these are concluded in Section 4.

2. Model

2.1 Friedel criterion

If an impurity dissolves in a matrix in the positively charged state, it attracts the conduction electrons by its strong Coulomb field and thus the impurity becomes screened [7]. If the screening is due to the formation of a bound state, the effective charge on the impurity changes. We examine the possibility of the bound state in the Friedel criterion: if the origin of energy is defined as the energy of an electron at rest outside the metal, the bottom of the conduction band in the metal has the negative energy E_0 given as [8]

$$E_0 \approx E_s + E_1 + \frac{3}{5} E_F + E_{xc}, \quad (1)$$

where E_s is the sublimation energy, E_1 the first ionization potential, $\frac{3}{5}E_F$ the average kinetic energy, E_F the Fermi energy, and E_{xc} the exchange-correlation energy of conduction electrons.

The energy required to liberate the i -th electron in the matrix is approximately

$$E_1 \approx E_i + E_{xc}, \quad (2)$$

where E_i is the i -th ionization potential of the impurity atom. E_{xc} is the same in (1) and (2).

If $E_i \gg E (= E_0 - E_{xc})$, the bound state i will exist and the corresponding electron will not be liberated in the matrix. If $E_i < E$, the i -th impurity electron will be liberated in the conduction band of the matrix. This criterion is used to estimate the effective valency, Z_I , of the impurity which gives the effective host and impurity valence difference as

$$Z_0 = Z_I - Z_H, \quad (3)$$

where Z_H is the host atom ionicity.

2.2 Size effect

The introduction of a defect in a metal displaces the host atoms from their equilibrium positions. Blatt [9] and Harrison [10] suggested that the effect of dilation is to change the ionic charge density in the vicinity of the defect, therefore, the effective charge on the defect changes and is given as

$$Z_{\text{eff}} = Z_0 - \frac{3}{\gamma_E} \frac{1}{a} \frac{da}{dc} Z_H. \quad (4)$$

Here $\gamma_E = 3(1 - \sigma)/(1 + \sigma)$, σ is Poisson's ratio and $(1/a) da/dc$ the relative change in lattice parameter (in %/at% impurity). The dilation may be positive or negative, therefore, the positive charge on the defect may decrease or increase.

2.3 Nonlinear screening

The screening of the impurity charge Z_{eff} by conduction electrons is carried out in the Hohenberg-Kohn [11] and Kohn-Sham [12] density functional formalisms.

The impurity-induced electronic charge density is given as

$$\delta n(\mathbf{r}) = \sum_{\epsilon_i < \mu} |\psi_i(\mathbf{r})|^2 - n_0, \quad (5)$$

where μ is the electron chemical potential, $n_0 = 3/4\pi r_s^3$ the mean electron density, and r_s the interelectronic distance. ε_i and $\psi_i(\mathbf{r})$ are the eigenvalues and eigenfunctions which are obtained by solving the Schrödinger equation

$$[-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r})]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}), \quad (6)$$

where

$$V_{\text{eff}}(\mathbf{r}) = -\frac{Z_{\text{eff}}}{r} + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{\text{xc}}(\mathbf{r}) \quad (7)$$

and

$$Z_{\text{eff}} = \frac{2}{\pi} \sum_{l=0}^{\infty} (2l+1) \delta_l(k_F). \quad (8)$$

$V_{\text{xc}}(\mathbf{r})$ is the functional derivative of a universal exchange and correlation energy functional of the particle mean density and is calculated in the same manner as done by Popovic et al. [13]. $\delta_l(k_F)$ are the l -th phase shifts at the Fermi surface with Fermi momentum k_F . Equations (5) to (8) are solved self-consistently. Approximate self-consistency is achieved by taking a screened Coulomb host-impurity potential

$$V_{\text{sc}}(\mathbf{r}) = -\frac{Z_{\text{eff}} e^{-\alpha r \beta}}{r}, \quad (9)$$

where the parameters α and β are chosen such that the correct amount of charge is displaced by $V_{\text{sc}}(\mathbf{r})$ and the potential generated by (7) self-consistently. The Schrödinger equation is solved numerically by integrating the radial wave equation for seven partial waves and the displaced charge is calculated by the Friedel sum rule given by (8).

Table 1

Physical parameters for Al alloys

impurity	Z_I	Z_0	$(1/a)da/dc$	ΔZ	Z_{eff}	Δq ($\mu\Omega\text{cm/at}\%$)		n_{ws}
						theor.	exp.	
Cu	1.0	-2.0	-0.092	-0.559	-1.441	0.46	0.89	1.24
Ag	1.0	-2.0	0.023	0.14	-2.14	0.71	1.08	1.67
Li	1.0	-2.0	-0.012	-0.07	-1.93	0.64	—	1.55
Cd	1.0	-2.0	-0.09	-0.547	-1.453	0.47	0.51	1.25
Mg	2.0	-1.0	0.099	0.60	-1.60	0.52	0.36	1.35
Zn	1.0	-2.0	-0.013	-0.079	-1.921	0.64	0.24	1.547
Be	1.0	-2.0	-0.672	-4.096	2.086	1.05	—	1.848
Ga	1.0	-2.0	0.045	0.274	-2.274	0.76	0.22	1.741
In	1.0	-2.0	0.0	0.0	-2.0	0.66	—	1.593
Ge	1.0	-2.0	0.045	0.274	-2.274	0.76	0.79	1.741
Si	1.0	-2.0	-0.042	-0.255	-1.745	0.57	0.60	1.441
Sn	2.0	-1.0	0.14	0.864	-1.864	0.62	—	1.514

Z_0 is the difference between the effective impurity valency Z_I and the valency Z_H of the matrix, $(1/a) da/dc$ the fractional change in lattice parameter, ΔZ ($= 3/\gamma_E (1/a) da/dc Z_H$) the charge due to size effect, $Z_{\text{eff}}e$ the total charge on the impurity including both Z_0e and $\Delta Z e$, Δq the residual resistivity in $\mu\Omega\text{cm/at}\%$, and n_{ws} the total electronic charge in the impurity Wigner-Seitz cell

Table 2
The screened Coulomb potential parameters α and β and phase shifts evaluated at the Fermi surface ($k = k_F$) for various impurities in Al matrix

para- meter	impurity											
	Cu	Ag	Li	Cd	Mg	Zn	Be	Ga	In	Ge	Si	Sn
α	0.5015	0.4266	0.4465	0.5003	0.4823	0.4474	1.3076	0.4148	0.4397	0.4148	0.4658	0.4232
β	1.6345	1.6931	1.6768	1.6348	1.6486	1.6760	1.0367	1.7030	1.6823	1.7030	1.6615	1.6714
δ_0	-0.9383	-1.2251	-1.1455	-0.9438	-1.0095	-1.1420	2.0710	-1.2735	-1.1726	-1.2735	-1.0710	-1.1194
δ_1	-0.2907	-0.4407	-0.3962	-0.2934	-0.3253	-0.3943	0.2905	-0.4687	-0.4111	-0.4687	-0.3566	-0.3821
δ_2	-0.0682	-0.1201	-0.1036	-0.0690	-0.0792	-0.1030	0.0519	-0.1310	-0.1091	-0.1310	-0.0897	-0.0986
δ_3	-0.0125	-0.0243	-0.0204	-0.0127	-0.0149	-0.0202	0.0091	-0.0271	-0.0217	-0.0271	-0.0172	-0.0192
δ_4	-0.0021	-0.0041	-0.0034	-0.0021	-0.0025	-0.0034	0.0017	-0.0046	-0.0036	-0.0046	-0.0028	-0.0032
δ_5	-0.0003	-0.0005	-0.0004	-0.0003	-0.0004	-0.0004	0.0000	-0.0006	-0.0005	-0.0006	-0.0004	-0.0004

3. Calculations and Results

The physical parameters used in the present calculations for various dilute alloys of Al are presented in Table 1. The effective charge on the impurity is calculated using (4). The values of $(1/a) da/dc$ are taken from the tables of Pearson [14]. For some of the impurities, the lattice dilation data in Pearson's tabulation is not proportional to the concentration. For such alloys the lattice dilation is calculated by taking the average of all the tabulated values. Out of the twelve impurities under investigation, the binding of electrons is accounted for in Cd, Zn, Ga, Ge, Si, Be, and Sn impurities and all the impurities except Be are found to be negatively charged.

3.1 Host-impurity potential and the phase shifts

The potential parameters α and β obtained self-consistently are tabulated in Table 2. The first six corresponding phase shifts evaluated at k_F are also tabulated there. The phase shifts decrease rapidly with increasing l . $l = 0$ and 1 phase shifts are dominating. Therefore, the maximum contribution to the charge density arises from s- and p-wave scattering. The d-wave phase shifts are found to be almost less than 10% of the s-wave phase shifts. Higher-order phase shifts are found to be negligible. This conclusion is similar to that obtained by Deutz et al. [6].

The self-consistent effective impurity potential given by (7) is calculated for all the alloys. The results are presented for two typical AlCu and AlGe alloys by solid lines in Fig. 1. Qualitatively similar results are found for all other alloys, too. The magnitude of the potential decreases to negligible amounts beyond the Wigner-Seitz radius, although the Friedel oscillations persist up to $r = 15$ at. units. We also plotted the

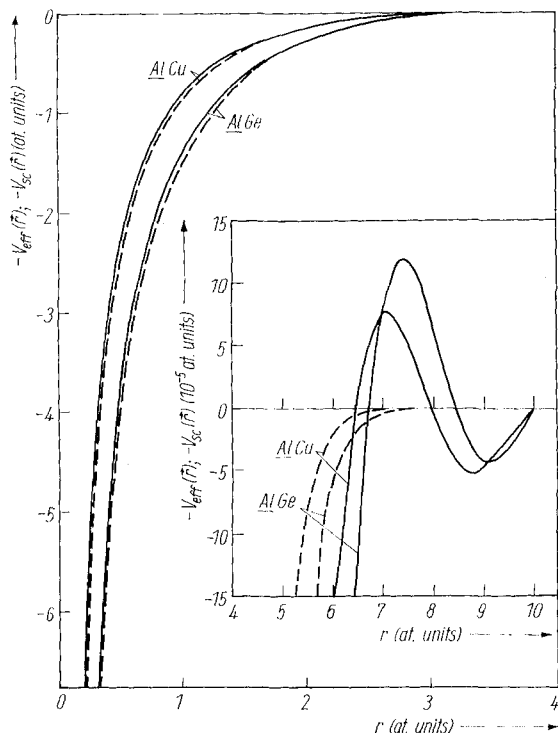


Fig. 1. The self-consistent potential $V_{\text{eff}}(\mathbf{r})$ (7) and $V_{\text{so}}(\mathbf{r}) = -(Z_{\text{eff}}/r) \exp(-\alpha r/\beta)$ vs. r for Cu and Ge impurities in a uniform electron gas of mean density appropriate to Al ($r_s = 2.07$). Solid and dashed lines represent $V_{\text{eff}}(\mathbf{r})$ and $V_{\text{so}}(\mathbf{r})$, respectively

values of $V_{sc}(r)$ given by (9) by dashed lines in the same figure for comparison. The two potentials are almost equal up to $r = 4$ at. units. At larger distances, $V_{sc}(r)$ decays exponentially while $V_{eff}(r)$ executes Friedel oscillations, although the amplitude of oscillations is quite small. The first and second nearest neighbour interactions always dominate in the binding of an impurity [7], therefore, the analytical expression given for $V_{sc}(r)$ may be useful for estimating other properties of the alloys.

3.2 Electronic charge distribution

The change in electronic charge distribution around impurities, $\delta n(r)/n_0$, is calculated. Typically we have shown in Fig. 2 the results for AlCu , AlSi , AlLi , and AlGa alloys where the impurities are negatively charged and for AlBe alloy where the impurity is positively charged. The Friedel oscillations, in the expected asymptotic form $r^{-3}\cos(2k_F r + \varphi)$, are exhibited in the inset. For AlBe there is a big pile-up of charge at the impurity site and the displaced charge density falls rapidly with the usual Friedel oscillations at large distances. An s-type bound state of energy 0.44171 at. units is also found in our calculations. The negatively charged impurities do not show any pile-up of charge in the vicinity of the impurity. Beyond 1 at. unit distance from the impurity, the charge density drops almost exponentially and shows Friedel oscillations at large distances. Similar characteristics of charge density are found for AlCd ,

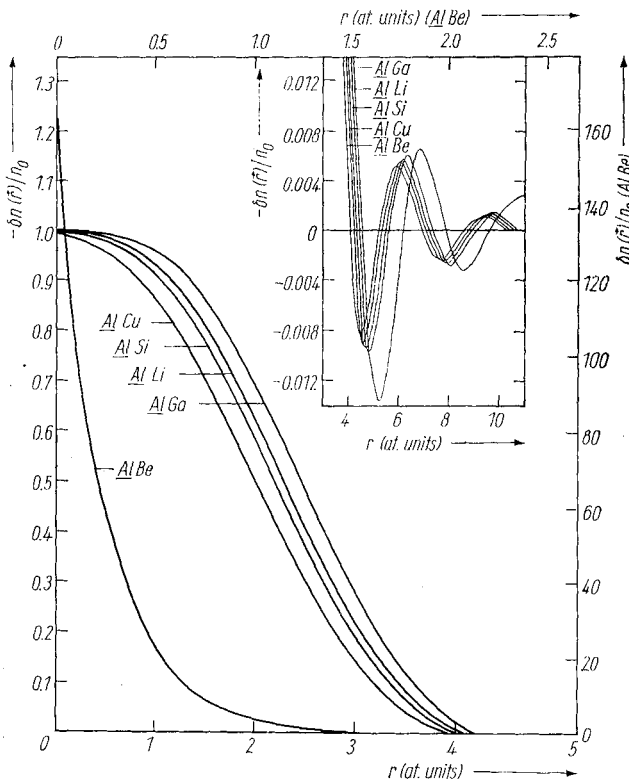


Fig. 2. $\delta n(r)/n_0$ vs. r (at. units) for Cu, Si, Li, Ga, and Be impurities in Al

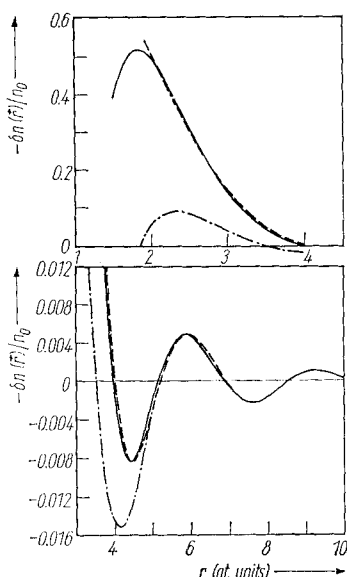


Fig. 3. Change in electronic charge density around Cu impurity in Al. Dashed line shows actual self-consistent calculations, while dash-dotted and solid lines represent results using Alfred and Van Osternburg's form and equation (10), respectively

ASn, AlIn, AlMg, AlZn, and AlAg alloys. Since $\frac{\delta n(\mathbf{r})}{n_0} = \frac{n(\mathbf{r}) - n_0}{n_0}$ and the minimum value of $n(\mathbf{r})$ can be zero, $\frac{\delta n(\mathbf{r})}{n_0}$ tends to -1 in the vicinity of $r \rightarrow 0$.

The change in electronic charge density around an impurity in the preasymptotic region is quite important for estimating the hyperfine field. Therefore, we made an attempt to fit the self-consistently calculated change in charge densities by an anal-

ytical expression

$$\delta n(\mathbf{r}) = C e^{-Dr^2} + \frac{A \cos(2k_F r + \varphi)}{r^3} + \frac{B \cos(2k_F r + \xi)}{r^4}. \quad (10)$$

The parameters A , φ , B , and ξ are evaluated in the same manner as done by Alfred and Van Osternburg [15] and used then in (10) to obtain C and D by the method of least-squares fit.

To show the validity of (10), we have plotted $\delta n(\mathbf{r})/n_0$ versus r in Fig. 3 for a representative AlCu alloy. Evidently Alfred and Van Osternburg's [15] $\delta n(\mathbf{r})$ given by the last two terms of (10) deviates from the self-consistent calculations almost completely for $r < 5$ at. units. However, (10) is in excellent agreement with the actual self-consistent calculation for $r > 2$ at. units. Since the Wigner-Seitz radius for the Al matrix is 2.98 at. units, (10) may be quite useful in evaluating the hyperfine field and related properties at the nearest neighbours. To reproduce $\delta n(\mathbf{r})$, we have tabulated the parameters A , B , C , D , φ , and ξ for various alloys in Table 3.

3.3 Charge transfer

We also calculated the total electronic charge in the impurity Wigner-Seitz cell. These values are tabulated in Table 1. If we compare these values with the effective impurity valency, we find that the Al matrix has substantially transferred the charge to the impurity Wigner-Seitz cell except for AlMg and AlSn alloys for which the charge is transferred to the matrix. As compared to the calculations of Deutz et al. [6], the charge transfer in our calculations is found to be larger because of the size effect and consideration of bound states. Flynn [16] and Martenson and Johansson [17] have shown that for the valence electrons a hole in a core shell can be described to a very good approximation by an impurity whose nuclear charge is increased by one. Flynn [16] calculated the positions of the bound 3d-type levels for Zn, Ga, and Ge impurities in Cu and Ag matrices in perfect agreement with the experimental measurements.

Table 3

A, φ , *B*, ξ , *C*, and *D* parameters of (10) for various impurities in Al matrix

impurity	parameter						
	Z_{eff}	<i>A</i>	φ	<i>B</i>	ξ	<i>C</i>	<i>D</i>
Cu	-1.441	0.02210	4.59065	0.04055	4.21658	-0.03759	0.28999
Ag	-2.14	0.02808	3.99099	0.06533	3.76749	-0.05680	0.26931
Li	-1.93	0.02634	4.14917	0.05803	3.89690	-0.05168	0.27667
Cd	-1.453	0.02193	4.55160	0.04236	4.19861	-0.03885	0.29352
Mg	-1.60	0.02335	4.42030	0.04705	4.10582	-0.04294	0.28827
Zn	-1.921	0.02626	4.15624	0.05772	3.90246	-0.05145	0.27698
Be	2.086	0.06057	-0.44991	0.05693	1.99832	0.01804	0.29910
Ga	-2.274	0.02915	3.89494	0.07011	3.68738	-0.05985	0.26463
In	-2.0	0.02693	4.09529	0.06044	3.85335	-0.05344	0.27425
Ge	-2.274	0.02915	3.89494	0.07011	3.68738	-0.05985	0.26463
Si	-1.745	0.02470	4.29743	0.05186	4.01433	-0.04686	0.28317
Sn	-1.864	0.02576	4.20106	0.05578	3.93835	-0.04999	0.27897

The contributions of these bound states in the core holes is carefully considered in the present calculations.

3.4 Residual resistivity

As a test of our calculations, we estimated the residual resistivity, $\Delta\rho$, for Al alloys using the phase shifts tabulated in Table 2, with the help of the expression [9]

$$\Delta\rho = 2.732 \frac{1}{k_F Z_H} \sum_{l=0}^{\infty} (l+1) \sin^2 (\delta_l - \delta_{l+1}), \quad (11)$$

where k_F is in at. units and $Z_H = 3$ is used for Al matrix. These results along with the available experimental values are tabulated in Table 1. A reasonable agreement is found between the calculated and experimental values for AlAg, AlCd, AlMg, AlGe, and AlSi. The results for AlZn and AlGa alloys are greater than the experimental values, while it is lower for AlCu. It is to be mentioned here that the second ionization potential E_2 for Zn is 17.8 eV, while E_0 for the Al matrix is 15.4 eV. The difference between E_2 and E_0 is only 2.4 eV. If this is to be regarded as uncertainty in the estimation of E_0 and E_2 , the effective valency of Zn in Al will become two instead of one. This will lead to $\Delta\rho = 0.26 \mu\Omega\text{cm/at}\%$ for AlZn alloy in good agreement with the experimental value. We also estimated the residual resistivity for AlLi, AlBe, AlIn, and AlSn alloys for which experimental data is not available. The estimated residual resistivity is appreciable for these alloys, therefore, these may be interesting samples to be investigated.

4. Conclusion

A simple but realistic physical model is adopted for the screening of an impurity due to the formation of bound states, lattice relaxation, and nonlinearity of the Fermi gas. The calculated phase shifts, residual resistivities, and charge transfers are found in good agreement with other calculations as well as with the experimental results

wherever available. The analytical expressions for the host-impurity potential and the change in charge distribution especially in the preasymptotic region may be quite useful for further investigations.

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