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Low-temperature thermopower of Al-based dilute alloys

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Abstract. We report systematic calculations of the low-temperature diffusion thermopower of Al-based dilute alloys with 3d and 4sp impurities, by solving self-consistently the linearized Boltzmann equation. The impurity scattering is described by the phase shifts obtained from self-consistent local-density-functional impurity-in-jellium calculations. Moreover, the influence of the full anisotropy of the Al Fermi surface on the scattering process is taken into account within the on-Fermi-sphere approximation. Our results explain successfully the experimentally measured variations in the thermoelectric power, except for Mn impurities. In this case, the presence of a narrow many-body resonance at the Fermi level in the localized-spin-fluctuations regime seems to be responsible for the large negative value of thermopower observed.

1. Introduction

The thermoelectric power of dilute alloys at low temperatures consists of the phonon drag contribution which is proportional to T^3 , and the so-called diffusion term which varies linearly with temperature. The diffusion thermopower reflects the energy derivative of the scattering amplitude of the Fermi surface (FS) electrons by the impurity potential and constitutes a very sensitive probe for studying the energy dependence of the scattering process.

The investigation of the low-temperature thermoelectric properties of Al-based dilute alloys has attracted considerable experimental interest [1–7]. It was found that the diffusion thermopower coefficient strongly depends on the specific type of the impurity and it is generally independent of the impurity concentration.

Model calculations of the low-temperature diffusion thermopower of 3d impurities in Al have been reported by Zlatic and Rivier [8]. These calculations rely on the Friedel–Anderson [9, 10] virtual-bound-state model and use the localized-spin-fluctuations approximation [11] in order to account for the large negative thermopower values measured for the impurities of the middle of the 3d series. The parameters involved in these calculations were fitted to the experimental resistivity values.

An attempt to calculate the thermoelectric power of Al-based dilute alloys starting from a self-consistent solution of the linearized Boltzmann equation using an anisotropic transport relaxation time was made by Böning [6]. In this approach, the Al host was described by the four-orthogonal-plane-wave (4-OPW) model [12] and the effective potential of the point defect by pseudopotential form factors. The scattering was treated using the first-order Born approximation. However, application of this method is restricted to sp impurities, where the weak scattering justifies the use of the Born approximation.

As a generalization of the above procedure, an effective T-matrix can be employed to describe the scattering, and the transition amplitude between two states on the FS is then

obtained in terms of the phase shifts, utilizing the so-called 'on-Fermi-sphere approximation' [13]. Within this approximation the phase shifts can be determined independently, e.g. by a first-principles calculation [14–16]. Thus, weak sp as well as strong d scattering can be treated on the same footing. This method is employed in the present article to calculate the diffusion thermopower of Al-based dilute alloys containing 3d and 4sp impurities, without using any adjustable parameter. We utilize the 4-OPW model for the FS of Al, whereas the phase shifts describing the impurity scattering are obtained from self-consistent impurity-in-jellium calculations within the framework of the density-functional theory [17]. The linearized Boltzmann equation is then solved self-consistently to evaluate the anisotropic transport relaxation time on constant-energy surfaces in the vicinity of the Fermi level. From this relaxation time the thermoelectric power is calculated.

In section 2 we describe our theoretical method and section 3 deals with some technical aspects of the computation. In section 4 we present and discuss our results.

2. Theory

The determination of the residual resistivity and the thermopower of dilute alloys requires the solution of the linearized Boltzmann equation in the presence of a homogeneous electric field \mathbf{E} and a temperature gradient ∇T [18]:

$$\left(-\frac{\partial f_k^0}{\partial E_k}\right) \mathbf{v}_k \cdot \left[e \left(\mathbf{E} - \frac{1}{e} \nabla \zeta \right) + \frac{E_k - \zeta}{T} (-\nabla T) \right] = - \sum_{k'} (g_{k'} - g_k) P_{kk'} \quad (1)$$

where g_k is the deviation from the Fermi–Dirac distribution function f_k^0 , $\mathbf{v}_k = \nabla_k E_k / \hbar$ is the group velocity of Bloch electrons, ζ is the chemical potential and $P_{kk'}$ is the scattering probability rate between states $|k\rangle$ and $|k'\rangle$. In the low-field limit and at sufficiently low temperatures, the incoherent scattering of conduction electrons from isolated impurity atoms is the dominant mechanism. Assuming elastic scattering we have

$$P_{kk'} = \frac{2\pi Nc}{\hbar} |T_{kk'}|^2 \delta(E_k - E_{k'}) \quad (2)$$

where N is the total number of atoms in the crystal, c is the atomic concentration of impurities and $T_{kk'}$ is the T-matrix describing the scattering by a single impurity atom.

In the low-field limit the vector mean free path Λ_k is defined by the linear *ansatz*

$$g_k = \left(-\frac{\partial f_k^0}{\partial E_k}\right) \Lambda_k \cdot \left[e \left(\mathbf{E} - \frac{1}{e} \nabla \zeta \right) + \frac{E_k - \zeta}{T} (-\nabla T) \right] \quad (3)$$

and is in general not parallel to the group velocity. However, following Böning *et al* [19] we assume that

$$\Lambda_k = \mathbf{v}_k \tau_k \quad (4)$$

where τ_k is the anisotropic transport relaxation time. Therefore, within the above approximations, equation (1) can be readily solved, yielding the following integral equation for τ_k :

$$\tau_k \mathbf{v}_k \frac{\Omega Nc}{4\pi^2 \hbar^2} \int_{\text{FS}} \frac{dS_{k'}}{v_{k'}} |T_{kk'}|^2 = \mathbf{v}_k + \frac{\Omega Nc}{4\pi^2 \hbar^2} \int_{\text{FS}} \frac{dS_{k'}}{v_{k'}} \tau_{k'} \frac{\mathbf{v}_k \cdot \mathbf{v}_{k'}}{v_k} |T_{kk'}|^2 \quad (5)$$

where k lies on the FS, Ω is the volume of the crystal and $v_k = |v_k|$.

On the other hand, substituting the form (3) for g_k into the general expression

$$j = \frac{2e}{\Omega} \sum_k v_k g_k \tag{6}$$

for the electric current density, we obtain for a crystal of cubic symmetry

$$j = \left[\frac{e^2}{12\pi^3\hbar} \int dE_k dS_k \left(-\frac{\partial f_k^0}{\partial E_k} \right) v_k \tau_k \right] \left(E - \frac{1}{e} \nabla \zeta \right) + \left[\frac{e}{12\pi^3\hbar T} \int dE_k dS_k \left(-\frac{\partial f_k^0}{\partial E_k} \right) (E_k - \zeta) v_k \tau_k \right] (-\nabla T). \tag{7}$$

In the absence of a temperature gradient, the response of the system is determined by the isothermal conductivity σ , which is given by the term in the first square brackets of (7). The second term in (7) gives the contribution of the temperature gradient to the current density. At low temperatures we can restrict ourselves to the leading order of a temperature power series expansion [18] and obtain

$$j = \sigma(E_F) \left(E - \frac{1}{e} \nabla \zeta \right) + \frac{\pi^2 k_B^2 T}{3e} \left[\frac{\partial \sigma(E)}{\partial E} \right]_{E=E_F} (-\nabla T) \tag{8}$$

with

$$\sigma(E) = \frac{e^2}{12\pi^3\hbar} \int_{E_k=E} v_k \tau_k dS_k. \tag{9}$$

Obviously, $\sigma(E_F) \equiv \sigma$. If we establish a temperature gradient in a specimen which is an open circuit ($j = 0$), the ratio of the observed EMF to the temperature gradient defines the thermopower:

$$S = \frac{\pi^2 k_B^2 T}{3e} \left[\frac{\partial [\ln \sigma(E)]}{\partial E} \right]_{E=E_F}. \tag{10}$$

This equation is known as the Mott formula [20]. As has been recently shown [21], even for a fully interacting electron-phonon system, and including the inelastic nature of the electron scattering by the phonons, the electron diffusion thermopower is still given by the Mott formula plus a small correction term.

3. Method of computation

According to equations (9) and (10), knowledge of the energy dependence of the host and impurity properties is necessary to calculate the electron diffusion thermopower. In order to evaluate the energy derivative in (10), the surface integration involved in (9) has to be carried out over the FS and also over surfaces of constant energy near E_F . In this respect, we calculate the anisotropic relaxation time as a function of k on five surfaces of constant energy, namely $0.998E_F$, $0.999E_F$, E_F , $1.001E_F$ and $1.002E_F$, by self-consistently solving

the integral equation (5) on these surfaces, using an iterative procedure. Starting with Ziman's [18] approximation as an initial guess for τ_k , namely

$$\tau_k^{-1} = \frac{\Omega N c}{4\pi^2 \hbar^2} \int_{E_k=E} |T_{kk'}|^2 \left(1 - \frac{v_k \cdot v_{k'}}{v_k v_{k'}}\right) \frac{dS_{k'}}{v_{k'}} \quad (11)$$

we obtain an adequate convergence in τ_k in about five iterations in all cases examined.

We construct the constant-energy surfaces around E_F by employing the 4-OPW model, using the Fermi energy and the pseudopotential matrix elements which were fitted by Cole *et al* [15] to the de Haas-van Alphen experimental data of Coleridge and Holtham [22]. Following Böning [6] we neglect any energy dependence of the pseudopotentials. The constant-energy surfaces obtained exhibit the same features as the FS of Al. In the second Brillouin zone they have a free-electron-like portion with a slightly negative curvature, which covers most of the FS, and hole-like cylinders with a high positive curvature, just below the Brillouin zone boundaries. Moreover, in the third zone there are toroid-like portions with a high negative curvature. The energy-surface integrations involved in (5) and (9) are performed by generating a system of triangles using about 1000 points on the second zone and about 650 points on the third zone, and then applying a first-order integration rule within each triangle. Special care was taken in the highly curved regions of the surfaces, where a denser mesh was used. The group velocity at a point k is calculated analytically, taking advantage of the explicit form of the 4-OPW Bloch wavefunctions [23].

In order to calculate the transition matrix $T_{kk'}$ we use the 'on-Fermi-sphere approximation', according to which the crystal lattice pseudopotential is ignored during the scattering of the electrons by the impurity atom [13]. Therefore the problem is reduced to the evaluation of the phase shifts $\delta_\ell(E)$ which describe the scattering of the angular momentum components of a single plane wave from the impurity potential. These phase shifts are obtained by calculating the electronic structure of an isolated impurity in a jellium having the electron density of Al. Within this model, a substitutional impurity is described by excavating a spherical hole with the volume of the Al Wigner-Seitz cell ($V = 9\pi^2(\hbar^2/2mE_F)^{3/2}$) in the jellium positive background and inserting the nuclear charge of the impurity in the centre of this cavity. The electronic structure is calculated self-consistently within the framework of density-functional theory, using a Green function technique. Exchange and correlation effects are included through the local-density approximation (LDA) with the parametrization of Vosko *et al* [24]. The range of the perturbing impurity potential $S = 10$ au and the angular momentum cut-off $\ell_{\max} = 3$ are sufficient to obtain adequate convergence in all the cases examined. The calculated phase shifts satisfy the Friedel's [25] screening rule

$$\Delta Z = \frac{2}{\pi} \sum_{\ell=0}^{\ell_{\max}} (2\ell + 1) \delta_\ell(E_F) \quad (12)$$

where ΔZ is the valence difference between the impurity and host atoms, within a few per cent. Details of our method of calculation can be found elsewhere [26].

4. Results and discussion

If we assume a free-electron band structure and, consequently, a spherical FS of Al host, $\sigma(E)$ is given by [27]

$$\sigma^{-1}(E) = \frac{4\pi\hbar^2 c}{Ze^2(2mE)^{1/2}} \sum_{\ell} (\ell + 1) \sin^2[\delta_{\ell+1}(E) - \delta_{\ell}(E)] \quad (13)$$

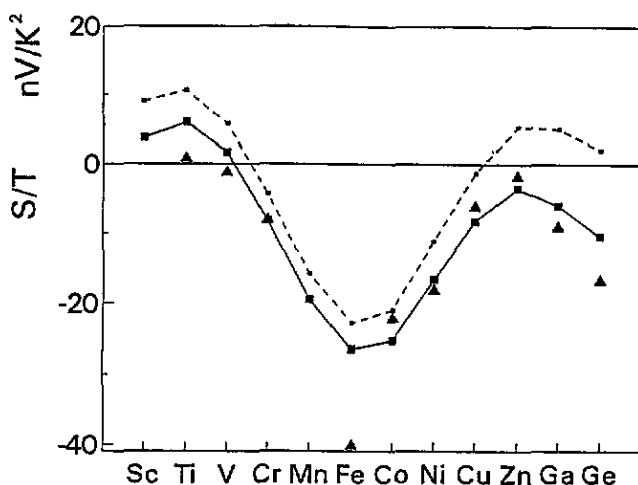


Figure 1. The low-temperature diffusion thermopower coefficient of 3d and 4sp substitutional impurities in an Al host: ■, theoretical results; ▲, experimental data [1-3, 6] (the experimental results for Mn were found to vary with the impurity concentration between -59 and -50 nV K^{-2} [1, 2] and are not presented in the figure); -■-, results obtained by the jellium model.

where Z is the valence of the host ($Z = 3$ for Al). Then, the electron diffusion thermopower can be calculated by substituting (13) into (10) and computing numerically the energy derivative involved. The results obtained for the thermoelectric power by this isotropic treatment of the impurity scattering are plotted in figure 1. We can see that, with the exception of Mn and Fe impurities, the theoretical results reproduce more or less the experimentally observed trends.

In the case of 3d impurities, the systematic variation in the low-temperature diffusion thermopower can be simply explained as follows. The resonant scattering of the d electrons from the impurity potential gives rise to the occurrence of a d virtual bound state. As a result, the excess density of states introduced by the impurity is dominated by an approximately Lorentzian-shaped peak, of half-width Γ , centred at E_d . This implies that the d resonant phase shift varies with energy as

$$\delta_2(E) = \tan^{-1} \left(\frac{\Gamma}{E_d - E} \right). \tag{14}$$

For the 3d impurities it is reasonable to assume that the impurity is essentially screened by the d electrons. Thus, we may neglect the contribution of all the other phase shifts, except for the d phase shifts in the vicinity of the Fermi energy. This finally leads to the following simple expression for the thermoelectric power:

$$S = \frac{\pi^2 k_B^2 T}{3|e|E_F} \left[\frac{E_F}{\Gamma} \sin \left(\frac{2\pi \Delta Z}{10} \right) - \frac{1}{2} \right]. \tag{15}$$

Equation (15) predicts for S/T a sinusoidal variation within the 3d series, rigidly shifted to the negative values owing to the presence of the second term in the square brackets. This behaviour is, indeed, qualitatively observed in figure 1.

As can be seen from figure 1, when the full anisotropy of the Al FS is taken into account in the calculation, much better agreement with the experiment is obtained. The

agreement is considerably improved, especially for the sp impurities. However, in the case of a Mn impurity, and to a lesser degree in the case of Fe, the theory cannot account for the large negative values of the experimentally measured diffusion thermopower coefficient. Considering the good general agreement between our results and the experiment, we believe that this discrepancy is ascribable to many-body correlation effects which are not taken into account in an LDA approach.

The low- and room-temperature experimental data probing the properties of the 3d impurities in Al suggest that the impurities are non-magnetic [28–30]; this is, in fact, what we have assumed in our calculations. However, when experiments show no sign of magnetism, the question is: does an impurity moment actually not exist, or is it screened by correlations with the conduction electrons (or very rapidly fluctuating) and thus cannot manifest itself? In order to answer this question, we performed spin-polarized calculations for all the impurities in Al. We find that in the case of Cr, Mn and Fe the calculations converge to magnetic solutions. This result is consistent with that obtained by the Korringa–Kohn–Rostoker (KKR) Green function method [31]. The KKR calculations yield also spin-polarized solutions for Cr, Mn and Fe impurities in Al. For Mn, KKR and jellium calculations give very similar local moments ($2.53\mu_B$ and $2.41\mu_B$, respectively). However, owing to band-structure effects, which are not included in our impurity-in-jellium approach, the impurity moment, as evaluated by the KKR method, is somewhat smaller for Cr ($2.00\mu_B$) and larger for Fe ($1.78\mu_B$) than our results ($2.34\mu_B$ and $1.20\mu_B$, respectively). On the other hand, density-functional calculations for Fe in Al, by the embedded-cluster method, showed that the impurity is non-magnetic if lattice relaxation effects are taken into account [32]. In order to study the energy stability of the magnetic impurity states, we calculated the magnetic exchange energy of the impurities. This can be done efficiently by carrying out constrained density-functional calculations. Applying this method, details of which can be found elsewhere [33], we obtain a magnetic energy of 0.46 eV for Cr, 0.60 eV for Mn and 0.06 eV for Fe impurities. It seems therefore that, although the magnetic state of Fe is quite sensitive to the various approximations involved in a theoretical calculation, a Mn impurity is clearly magnetic in Al.

It should be mentioned that LDA calculations provide a static picture of the ground-state properties of a system, within the framework of a one-electron theory. A spin-polarized impurity state has, in this context, a well defined spin with infinite lifetime. On the other hand, Al–Mn is considered as a typical example of a spin-fluctuating system [29, 30]. The central concept of the theory of localized spin fluctuations is the existence of a local moment which fluctuates with a lifetime τ_{sf} and only when the temperature is higher than a characteristic temperature $h/k_B\tau_{sf}$ does the conduction electron, as a probe, not have the time to see that the impurity moment is ephemeral. This characteristic temperature is estimated to be of the order of 900 K for Al–Mn [29], which places this system in the spin-fluctuating regime at low temperatures and room temperature. In this regime, the density of states of a magnetic impurity is characterized, in addition to the single-particle double-peak structure, by the presence of a many-body resonance peak, of Abrikosov–Suhl type, at the Fermi level [29, 30]. This narrow resonance is presumably responsible for the large negative value of the diffusion thermopower observed [8].

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