Impurity Scattering in Dilute Silver Alloys

P. T. Coleridge
National Research Council, Ottawa, Canada

and

Martin J. G. Lee*
The James Franck Institute and the Department of Physics, The University of Chicago, Chicago, Illinois 60637

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Phase shifts that describe the scattering of conduction electrons by impurity atoms incorporated substitutionally in a silver lattice have been deduced from experimental Dingle-temperature data. The results are consistent with a Friedel model of the electronic structures of the impurity states.

In contrast to the wealth of information now available concerning electronic states in pure metals, impurity states in dilute alloys have been relatively little studied. Nevertheless, measurements of the concentration dependence of the extremal cross-sectional areas of the Fermi surface, and of the impurity scattering rates for extremal orbits, are expected to yield important information concerning the electronic states of the impurity atoms. Previous analyses of the scattering anisotropy[1] either have been empirical descriptions or have used approximate models to evaluate the phase shifts characterizing the impurity states. A recent attempt to overcome this problem[2] failed because of the unknown renormalization of the charge density around the impurity. The purpose of this Letter is to show how the impurity states in dilute alloys can be determined from the Dingle-temperature anisotropies, and to illustrate the method by considering two silver alloys, Ag(Au) and Ag(Sn).

At a point $\vec{k}$ on the Fermi surface, the inverse relaxation time due to impurity scattering is given by[2,3]

$$1/\tau(\vec{k}) = -(2c/\hbar)\operatorname{Im} T_{\vec{k}\vec{k}}, \tag{1}$$

where c is the fractional impurity concentration. If the scattering center is assumed to be confined to a single atomic cell, the forward-scattering element of the T matrix can be written in the form

$$T_{\vec{k}\vec{k}} = -\sum_l t_{\vec{k}}^{\,l} S_l, \tag{2}$$

where the $t_{\vec{k}}^{\,l}$ are real coefficients which depend on the partial-wave components of the host-metal wave functions. We have introduced the scattering parameters

$$S_l \equiv \{A_l \sin(\eta_l^{\,i} - \eta_l^{\,h}) \exp[i(\eta_l^{\,i} - \eta_l^{\,h})]\}, \tag{3}$$

where the A_l are complex k-independent renormalizing coefficients which differ from unity only if the primary scattered wave is appreciably backscattered by the host lattice, and where η^i and η^h are impurity- and host-metal phase shifts, respectively. It has been shown elsewhere that the scattering phase shifts for a pure metal can be determined by analysis of experimental Fermi-surface anisotropies,[4] and that the coefficients $t_{\vec{k}}^{\,l}$ can be deduced very readily from the results of such a phase-shift analysis for the host metal.[5] Integrating Eqs. (1) and (2) around an extremal orbit yields an expression for the Dingle temperature X:

$$X = (\hbar^2 c/2\pi^2 k_B m_c)\sum_l (\partial\mathcal{A}/\partial\eta_l)_{E_F} \operatorname{Im} S_l, \tag{4}$$

where k_B is Boltzmann's constant, and m_c is the cyclotron mass of the orbit. The coefficients $(\partial\mathcal{A}/\partial\eta_l)_{E_F}$, the derivatives of the area of the orbit with respect to the phase shift at a constant value of the Fermi-energy parameter E_F, can also be deduced very readily from the results of a phase-shift analysis for the host metal.[5]

Brown and Myers[6] have measured Dingle temperatures for extremal orbits in several dilute silver-based alloys. Their most reliable results are for Ag(Au) and Ag(Sn), of which several samples of different concentrations were studied. The concentrations of the Ag(Sn) samples have recently been redetermined from their residual resisitivities, and in the present calculations we have used these revised results.[7] By making a least-squares fit based on Eq. (4) to the Dingle temperature data for the (100) and (111) "belly orbits," the (100) "rosette," the (110) "dog's bone," and the (111) "neck," using Halse's experimental values for the cyclotron masses,[8] we have determined the scattering parameters $\operatorname{Im} S_l$ for these two alloys. The experimental data and

TABLE I. Experimental Dingle temperatures in dilute silver alloys (°K/at.%), and scattering parameters deduced from the data.

Orbit	Ag(Au) Expt.	Ag(Au) Fit	Ag(Sn) Expt.	Ag(Sn) Fit
$B\langle 100\rangle$	8.7(2)	8.74	150(15)	145
$B\langle 111\rangle$	8.7(2)	8.79	137(8)	139
$R\langle 100\rangle$	7.0(10)	6.96	150(15)	161
$D\langle 110\rangle$	7.0(10)	6.96	179(8)	171
$N\langle 111\rangle$	3.6(2)	3.72	213(8)	202
rms error of fit	0.1		8	
$\mathrm{Im}S_0$	0.050(5)		0.03(20)	
$\mathrm{Im}S_1$	0.009(2)		0.58(4)	
$\mathrm{Im}S_2$	0.0065(6)		0.05(4)	

our results are shown in Table I. On physical grounds we have assumed a small amount of d scattering in Ag(Sn), although this is not required by the least-squares fit. Our results show that impurity scattering is predominantly s like in Ag(Au) and p like in Ag(Sn). Contours of constant inverse relaxation time, calculated from the scattering parameters using Eqs. (1) and (2), are shown in Fig. 1. Empirical inversions of the Ag(Au) data, and of the earlier Ag(Sn) data, were published in Ref. 6.

In order to deduce the impurity phase shifts for these alloys, it is necessary to obtain information about the coefficients A_l. One important constraint is imposed by the optical theorem[9]:

$$\mathrm{Im}\,T_{\vec{k}\vec{k}} = -(8\pi^2)^{-1}\int |T_{\vec{k}\vec{k}'}|^2\, dS_{k'}/\hbar v_{k'}. \qquad (5)$$

Using the formalism of Ref. 3, a general element of the T matrix can be expressed in the form [cf. Eq. (2)]

$$T_{\vec{k}\vec{k}'} = -\sum_l t_{\vec{k}\vec{k}'}{}^l S_l, \qquad (6)$$

where the complex coefficients $t_{\vec{k}\vec{k}'}{}^l$ depend on the host-metal wave functions in the initial and final states, and the scattering parameters are given by Eq. (3). Thus the left-hand side of Eq. (7) is proportional to A_l [Eqs. (2) and (3)], whereas the right-hand side is proportional to $|A_l|^2$. By evaluating the Fermi-surface integral using wave functions determined from the phase-shift parametrization one obtains, for each value of l, a relationship between the real and the imaginary parts of A_l; and for a given value of $|A_l|$ it is generally possible to find a unique set of $|\eta_l{}^i - \eta_l{}^h|$ which is consistent with the Dingle-temperature data and which satisfies the optical theorem.

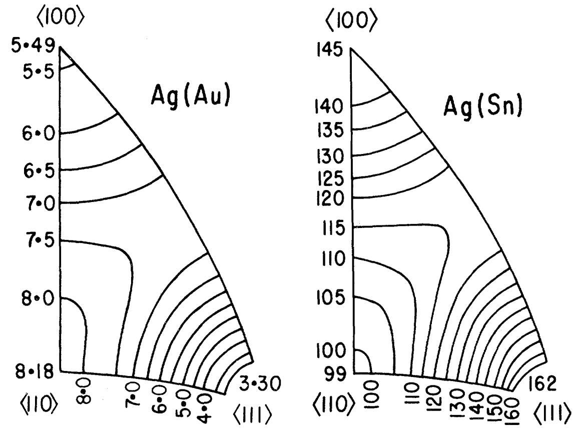

FIG. 1. Anisotropy of the inverse lifetime for impurity scattering in Ag(Au) and Ag(Sn). Contours of $(10^{-12}/\tau)$ sec^{-1} at.%$^{-1}$ derived from Dingle-temperature data as described in the text.

When an ion is inserted into a metallic lattice, the Coulomb field of the excess charge Z must be screened by displacement of conduction electrons. In order to achieve this, the impurity phase shifts must satisfy the Friedel sum rule, which for a spherical Fermi surface takes the form[10,11]

$$Z = \mathfrak{F} \equiv (2/\pi)\sum_l (2l+1)(\eta_l{}^i - \eta_l{}^h). \qquad (7)$$

For Ag(Sn) ($Z = 3$), the signs of the $\eta_l{}^i - \eta_l{}^h$ can be determined from this further constraint. For Ag(Au) ($Z = 0$) an ambiguity remains, which can be resolved by comparison with the phase shifts for pure silver and pure gold. The correctness of this choice has been confirmed by calculating the resistivity of Ag(Au), which is sensitive to the signs of the phase shifts.

So far we have regarded the $|A_l|$ as convenient parameters in terms of which to discuss results. Harris[12] has shown that by a procedure related to band-structure calculations they can be calculated from a knowledge of host and impurity potentials. An alternative approach is to exploit the fact that the values of A_l for different impurities in a common host are not independent. Morgan[3] has shown that the A_l can be related to a matrix $T_{ll'}$, which describes backscattering of an outgoing spherical wave by the host lattice.[13] To be more precise, if a_l is the amplitude of the wave function in the pure host and $b_{l'}$ the amplitude of the spherical outgoing wave, then $A_l = 1 + \sum_{l'} T_{ll'} \times b_{l'}/a_l$. In the alloys considered here, scattering into f and higher partial waves is negligible. The s, p, and d partial waves transform according to

TABLE II. Best assessment of impurity-state parameters in Ag(Au) and Ag(Sn). $\Delta\eta_l \equiv \eta_l^i - \eta_l^h$.

		$\ell = 0$	$\ell = 1$	$\ell = 2$	$\mathfrak{F}$
		(present work)			
Ag(Au)	$\lvert A_\ell \rvert$	1.01	1.03	1.00	
	$\text{Im}\, A_\ell / \text{Re}\, A_\ell$	-.016	.026	-.042	
	$\Delta\eta_\ell$	.232	.082	-.062	0.11
Ag(Sn)	$\lvert A_\ell \rvert$	1.00	.85	1.00	
	$\text{Im}\, A_\ell / \text{Re}\, A_\ell$	-.014	.118	.119	
	$\Delta\eta_\ell$	.181	.916	.174	2.42
		(comparison with previous work)			
Ag(Au)[a]	$\Delta\eta_\ell$	.189	.005	-.025	0.05
Ag(Au)[b]	$\Delta\eta_\ell$	.496	.068	-.023	0.37
Ag(Sn)[c]	$\Delta\eta_\ell$	1.002	.908	.109	2.75
Ag(Sn)[d]	$\Delta\eta_\ell$	.437	.859	.185	2.50
		(host phase shifts for pure Ag and Au)			
Ag	η_ℓ^h	.179	.110	-.103	~0
Au	η_ℓ^h	.369	.133	-.160	~0
Ag(Au)	$\Delta\eta_\ell$	.190	.023	-.053	

[a] Ref. 15.
[b] Ref. 16.
[c] Ref. 17.
[d] Ref. 18.

different irreducible representations of the cubic group, and the matrix $T_{ll'}$ can be shown to be diagonal.[14] Then the A_l are given by

$$A_l = \frac{1 - iT_{ll} \sin\eta_l^h \exp(i\eta_l^h)}{1 - iT_{ll} \sin\eta_l^i \exp(i\eta_l^i)}, \tag{8}$$

where the complex coefficients T_{ll} are characteristic of the host lattice and independent of the impurity.

As the coefficients A_l for the two alloys cannot be determined uniquely from the Dingle-temperature data, they have been estimated [using Eq. (8)] from a single set of the coefficients T_{ll} for the silver lattice, assuming backscattering to be as weak as possible consistent with the data. The impurity-state parameters deduced in this way are presented in Table II.[15-18] It is interesting that the scattering phase shifts for Ag(Au) are in close agreement with phase shifts derived from the minimum perturbation form factors[19] for pure silver and pure gold. The Friedel sum is close to zero, as one would expect in view of the very similar atomic radii of the two metals. Huang[15] has estimated the scattering phase shifts for Ag(Au) using a model due to Mott,[20] in which the impurity is represented by a screened square potential well. His results are in qualitative agreement with our own, but his model potential underestimates the *p* and *d* components of impurity scattering. The *ab initio* calculation carried out by Brown and Morgan[16] is in somewhat better agreement with our results.

When an impurity is introduced which strains the lattice, the Friedel sum rule must be modified to take into account the change in the average ionic density. Blatt[17] has shown that, for Ag(Sn), the Friedel sum should be $\mathfrak{F} \approx 2.75$. Using the procedure of Alfred and van Ostenburg[21] to estimate the higher ($l \geq 3$) phase shifts, we find that these contribute ≈ 0.4 to the Friedel sum, bringing our Friedel sum ($\mathfrak{F} \approx 2.8$) into good agreement with Blatt's result. Our impurity phase shifts are in qualitative agreement with the results of calculations by Blatt,[17] based on a square-well model of the impurity potential, and by Alfred and van Ostenburg,[18] based on an interpretation of NMR data.

We have shown how impurity-scattering phase shifts of dilute alloys can be determined from Dingle-temperature data by taking into account the renormalization of the wave function on the impurity site due to backscattering by the host lattice. Our results represent a consistent microscopic interpretation of the Dingle-temperature anisotropies of the dilute silver alloys Ag(Au) and Ag(Sn) taking proper account of the band structure of the host. The derived impurity phase shifts satisfy the optical theorem and the Friedel sum rule, and are consistent with a single set of backscattering coefficients for the silver lattice. We have assumed that off-diagonal elements of the scattering matrix are negligible, and have taken the diagonal elements to be as weak as possible consistent with the data. An investigation of these assumptions from first principles will be the subject of further work.

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Evaluation of Mott's Parameters for Hopping Conduction in Amorphous Ge, Si, and Se-Si

D. K. Paul and S. S. Mitra
Department of Electrical Engineering, University of Rhode Island, Kingston, Rhode Island 02881

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The temperature dependence of electrical conductivity of rf-sputtered amorphous Ge, Si, and Ge-Si films as functions of annealing temperature and time have been investigated for $350 \gtrsim T \gtrsim 77$ K. Annealing shifts the hopping region to lower temperatures. We find that reasonable values of Mott's parameters are obtained only for properly annealed specimens in the true hopping-conduction region.

The band structure and transport properties of amorphous semiconductors have been subjects of increasing interest in recent years (for recent reviews and bibliographies, see Brodsky,[1] Tsay, Paul, and Mitra,[2] and others[3]). Though there is yet no agreement about a proper model for electron transport mechanisms,[1,3,4] certain basic experimental facts seem to be well established.[1,3]

From a series of extremely careful isothermal and step-annealing experiments we have investigated the annealing mechanisms of amorphous germanium,[5] Ge-Si (50% Ge and 50% Si), and Si