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Phonon-Drag Thermopower in Dilute Copper Alloys*

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The change in phonon-drag thermopower of copper with alloying is determined for several dilute copper alloys. Assuming a Rayleigh law for scattering of phonons by the solute atoms, with relaxation time $\tau_i=(a\omega^4)^{-1}$, the experimental results are used to obtain numerical values for the parameter a. These results are then compared with the values of a calculated for elastic sacttering of long-wavelength phonons by the mechanism of mass difference alone. Solute concentrations employed in this investigation are 0.03 at.% Au, 0.09 and 0.2 at.% Ag, and 0.44 at.% Si. For Cu-Au, the results indicate that phonons are scattered predominantly through the mass-defect mechanism. The Cu-Si data yield a contribution from the mass-defect term which is of the same magnitude as the contribution from other phonon-scattering mechanisms (lattice distortion). For Cu-Ag, the results indicate that phonons are scattered in this alloy predominantly by mechanisms other than mass difference. The relative magnitude of the lattice-distortion contribution is least in Cu-Au, increasing in Cu-Si and Cu-Ag in that order. The Cu-Si data are in agreement with previous results, while for Cu-Ag and Cu-Au, the results are in agreement with qualitative considerations based on the range of solid solubilities in these alloys.

I. INTRODUCTION

RECENT theoretical work in the transport properties of metals has resulted, among other things, in a general expression for the phonon-drag thermopower in pure metals.[1] Using this general expression,[1] Huebener[2] has obtained a relation for the change in phonon-drag thermopower due to point defects in a metal. These results have been applied to the attenuation of phonon-drag thermopower due to lattice vacancies in gold.[2] It is found, on assumption of a pure Rayleigh law for phonon scattering, that lattice vacancies in gold scatter phonons largely be means of the strain field associated with a vacant lattice site.[2] If, in the case of alloys, the solute atom may be treated as a point defect, and a pure Rayleigh-scattering law assumed, then the theory developed for lattice vacancies in gold can be applied to the scattering of phonons by solute atoms in dilute alloys. A program of this nature has already been carried out for Cu-Si and Cu-Al alloys.[3] Using the theory of Klemens[4] to interpret the experimental results, it was concluded that, for Cu-Al, phonon scattering can be attributed largely to the perturbation in mass periodicity caused by the presence of aluminum atoms in the copper host. In Cu-Si, the aforementioned contribution of mass deviation is found to be of the same magnitude as the combined contribution due to a change in force constants and the elastic strain field due to the solute atom.[3] The current work is an extension of the previous treatment to dilute alloys of gold and silver, respectively, in copper. At the same time, results and analysis are presented for an additional Cu-Si alloy. Attenuation of the phonon-drag component in copper-gold and copper-silver alloys has been previously observed,[5] complete quenching of the phonon-drag component being noted for 0.96 at.% silver and 0.4 at.% gold, respectively.[5] In the present case, analysis of phonon-drag attenuation along the lines used previously[3] requires that phonon scattering by impurities be small in comparison to the effects of other phonon-scattering mechanisms.[3] Hence the present solute concentrations are chosen to be markedly lower than those employed by previous investigators.[5] As in earlier work,[3] a major current objective lies in using the change in phonon-drag thermopower, with alloying, to obtain information regarding the mechanisms by which solute atoms scatter phonons in dilute copper alloys.

II. EXPERIMENTAL

The sample preparation and experimental techniques are essentially the same as those used previously.[3] One difference, in the present case, lies in the final anneal given all samples. For the pure copper and alloys used in the present work, the final vacuum anneal was carried out for 24 h at a temperature of 600°C, the vacuum being maintained at 10^{-6} Torr throughout the annealing operation. The starting materials were ASARCO 0.99999 purity, copper, silver and gold, while the silicon was Dow-Corning semiconductor grade

TABLE I. Residual resistivities, solute concentrations and values of the scattering parameter for dilute copper alloys.

Solute	At.% solute	Resistivity at 4.2°K ($\mu\Omega$ cm)	a from Eq. (4) (10^{-43} sec^3)	a_m from Eq. (8) (10^{-43} sec^3)
Au	0.03	0.021	1.3±0.5	0.93
Ag	0.09	0.017	5.6±1.9	0.31
Ag	0.2	0.029	15±6	0.68
Si	0.44	1.31	2.3±0.9	0.96

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(0.999999 purity). In all cases the finished product was in the form of 0.010-in.-diam wire. The annealed pure copper wires had a resistivity at 4.2°K of 2.09×10^{-3} $\mu\Omega$ cm. Solute content for the alloy wires, as determined by spectrochemical analysis, together with resistivities measured at 4.2°K, are listed in Table I. The experimental technique consisted of determining the emf generated by the alloy-copper thermocouple, as a function of temperature and differentiating this primary data to obtain ΔS, the difference in thermopower between the alloy and copper. Voltages generated by the alloy-copper thermocouples were determined by means of a Rubicon thermofree six-dial potentiometer with a resolution of 0.01 μV. A germanium resistance thermometer was used to determine temperature from 4.2 to 100°K, with a copper-constantan thermocouple in use above this latter temperature. The temperature measurements are estimated as accurate to 0.1°K.

III. TREATMENT OF DATA AND RESULTS

The method for obtaining ΔS_g, the change in phonon-drag thermopower with alloying, has been detailed previously.[5,3] Hence, for the alloys used in this work, only an outline is presented of the technique used in extracting ΔS_g from the data.

The change in phonon drag thermopower with alloying is obtained from the relation

$$\Delta S=\Delta S_e+\Delta S_g, \qquad (1)$$

where ΔS is the experimentally measured difference in thermopower between the alloy and pure copper; the computed difference in diffusion thermopower ΔS_e is given by

$$\Delta S_e=\frac{S_e^{\rm Cu}}{(W_e^0/W_e^1)+1}\left[\frac{S_e^1}{S_e^{\rm Cu}}-1\right], \qquad (2)$$

where $S_e^{\rm Cu}$ is the diffusion thermopower of pure copper, W_e^1 is the electronic thermal resistivity due to the solute and W_e^0 is the intrinsic electronic thermal resistivity of copper. The quantity S_e^1 is the characteristic thermopower of the solute in copper. The diffusion thermopower $S_e^{\rm Cu}$ is obtained from the Kohler equation[6]

$$S_e^{\rm Cu}=\textstyle\sum_i W_e^i S_e^i/\sum_i W_e^i, \qquad (3)$$

where W_e^i and S_e^i are the electronic thermal resistivity and characteristic thermopower due to the ith scattering agent in copper. In obtaining $S_e^{\rm Cu}$ from Eq. (3), the effects of trace amounts of iron, in causing a large negative peak at low temperatures, are taken into account using the data of Gold *et al.*[7] Figure 1 shows the measured thermopower of the pure copper, together with $S_e^{\rm Cu}$, the diffusion thermopower computed from Eq. (3). The difference between the two curves of Fig. 1 yields $S_g^{\rm Cu}$, the phonon-drag thermopower of copper. The absolute thermopower of copper was obtained by measuring ΔS for a copper-lead thermocouple, thence using the values given by Christian *et al.*, for the thermopower of lead.[8] In accordance with previous assumptions the phonon-drag thermopower of copper is assumed negligible at 320°K.[3,5] The measured change in thermopower for the copper-alloy thermocouples is shown in Fig. 2. Our interest lies solely in the phonon drag component for $T>80$°K, hence the alloy data is taken only over the temperature range from $T=78$ to 320°K. On the other hand, in order to account for the effects of iron,[7] the pure-copper data must be taken from

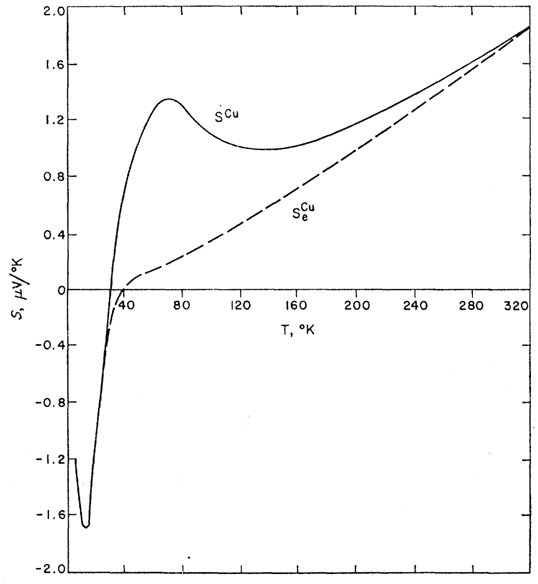

FIG. 1. Thermoelectric power of pure copper.

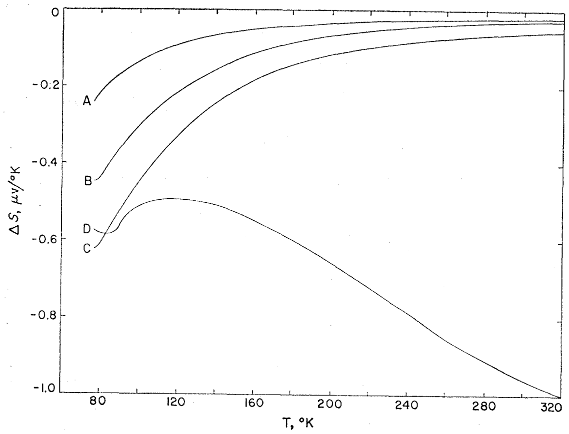

FIG. 2. ΔS, the difference in thermopower between the alloys and pure copper. A=0.03% Au, B=0.09% Ag, C=0.2% Ag, D=0.44% Si.

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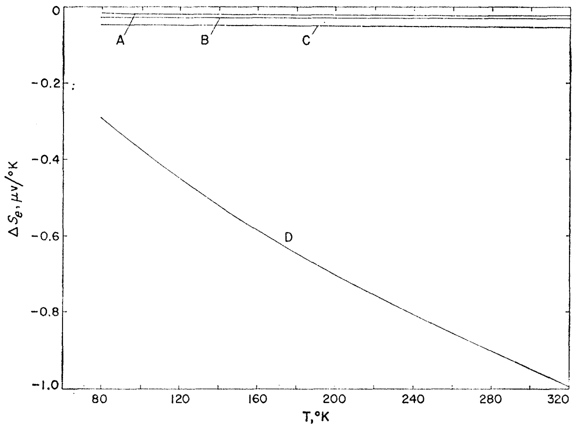

FIG. 3. ΔS_e, the difference in diffusion thermopower between the alloys and pure copper. Alloy identification (A,B,C,D) same as in Fig. 2.

4.2 to 320°K. Figure 3 shows ΔS_e for the alloys as computed from Eqs. (2) and (3). In Eq. (2) it is assumed that S_e^1 is proportional to temperature, hence determination of S_e^1 at 320°K is sufficient to determine this quantity over the entire range of temperatures.[5] Returning to Fig. 3 it is noted that ΔS_e for Cu-Ag and Cu-Au is small in agreement with previous results for higher concentrations.[5] In the Cu-Si alloy, the valence difference between solute and solvent is reflected in the relatively large value obtained for ΔS_e.[3] Figures 4 and 5 show ΔS_g obtained from Eq. (1).

IV. CALCULATIONS AND DISCUSSION

At temperatures where phonon-phonon collisions dominate in the pure metal,[2]

$$\Delta S_g = -Ae^{\beta/T}\int_0^{\Theta/T}\frac{Z^2e^Z dZ}{(e^Z-1)^2[1+b\hbar^2e^{-\beta/T}/ak^2Z^2T]}, \quad (4)$$

where $Z=\hbar\omega/kT$, ω being the phonon frequency, $\hbar$ is Planck's constant divided by 2π, Θ is the Debye temperature, and A, β, a, and b are constants. It is assumed, in obtaining Eq. (4) that τ_i, the relaxation time for phonon-impurity scattering in the alloy, and τ_0 the relaxation time for phonon-phonon scattering in the pure metal are of the form[2]

$$\tau_i^{-1} = a\omega^4, \quad (5)$$

$$\tau_0^{-1} = b\omega^2Te^{-\beta/T}. \quad (6)$$

The ω^4 dependency for τ_i^{-1} follows from the assumption of pure Rayleigh scattering.[2,4] The relaxation time τ_0 is essentially empirical and has been chosen to fit lattice thermal-conductivity data.[2,3,9]

An objective of the present work is the evaluation of a using Eq. (4). This can be accomplished by numerical integration provided that A, β, and b are known. The constants b and β have already been evaluated from the lattice thermal conductivity of pure copper.[3] The values obtained are, $b=4.19\times10^{-18}$ sec deg^{-1} and $\beta=43.6$°K.[3] At present there is little theoretical justification for the assumed form of the relaxation time shown in Eq. (6).[9] In fact, there is, *a priori*, no reason to believe that Eq. (6) is uniquely the best form of the relaxation time. Hence, at present, no physical significance can be attributed to the value obtained for β.[3] In the present case the overriding consideration has been that of obtaining a good fit to the T^{-1} dependency exhibited by the lattice thermal conductivity at temperatures above the conductivity maximum.[2,3,9]

The constant A is evaluated from the expression[2]

$$S_g^{\mathrm{Cu}} \approx Ae^{\beta/T}\int_0^{\Theta/T}\frac{Z^2e^Z dZ}{(e^Z-1)^2}. \quad (7)$$

Using the value of S_g^{Cu} at $T=90$°K, from Fig. 1, with $\Theta=310$°K,[10] it is found that $A=0.21$ μV/°K. The parameter a may now be evaluated from Eq. (4) by numerical integration using an IBM 7090 computer. The results are shown in Table I. The deviations shown have been computed from Eq. (4) using the estimated experimental error of ±0.05 μv/°K.

Consideration of elastic phonon scattering by point defects, in the long-wavelength limit, leads to theoretical relations for τ_i of the form given in Eq. (6).[4,11] The assumption of elastic scattering is restrictive in the sense that inelastic scattering leads to deviations from

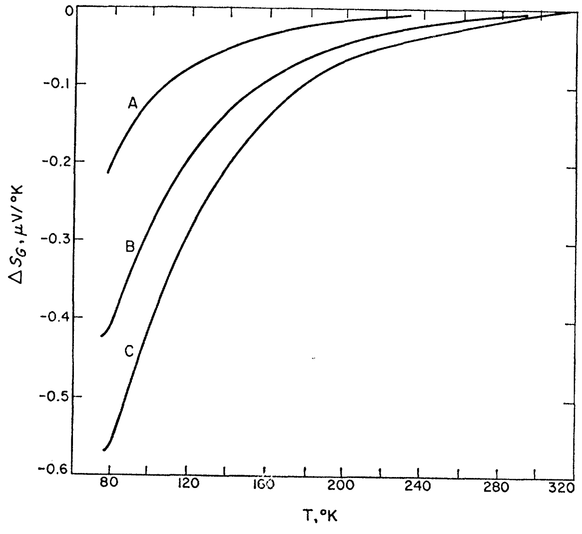

FIG. 4. ΔS_g, the difference in phonon drag thermopower between the alloys and copper. A=0.03% Au, B=0.09% Ag, C=0.2% Ag.

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a pure Rayleigh scattering law.[12,13] For the present case, in the theory leading to Eq. (4) a Debye spectrum is assumed.[2] Furthermore, it is assumed that the phonon spectrum is unchanged by alloying.[2] Consistent with these assumptions the simpler theory was used to calculate the scattering parameter for comparison with the current experimental values. Using the Klemens theory,[4] it is a relatively simple matter to calculate a for scattering of phonons by a substitutional impurity differing only in mass from the atoms of the host crystal. In addition, the theory[4] contains terms due to changes in force constants and the strain field associated with a point defect. However, the calculation for phonon-scattering mechanisms, other than mass difference, are relatively inexact. This is due partly to approximations in the theory[4] and partly, in the case of metals, to the difficulties associated with computing interatomic force constants.[14] Hence only the mass-difference mechanism is considered in the present calculation. The scattering parameter calculated in this way is designated by the symbol a_m. Thus[4]

$$a_m = (\Omega f / 4\pi v_s^3)[\Delta M/M]^2, \qquad (8)$$

where Ω is the atomic volume, f is the fraction of solute atoms present in the metal and v_s is the velocity of sound. M is the average mass for the atoms of the host crystal and ΔM is the difference in mass between the solute atoms and copper. The values calculated for a_m from Eq. (8) are shown in Table I. In obtaining these results the value used for v_s was 2.37×10^5 cm sec^{-1}.[3]

The mass defect term in Cu-Au lies reasonably close to the experimental value, while for Cu-Ag a considerable discrepancy exists. Comparing the calculated mass defect term to the experimental value, the relative contribution from lattice distortion[15] is lowest in Cu-Au, increasing in Cu-Si and Cu-Ag in that order. The present copper-silicon results indicate a contribution from lattice distortion which is of the same magnitude as the mass-defect term, in agreement with previous conclusions based on thermoelectric power[3] and lattice thermal conductivity.[16] For copper-gold, results from lattice thermal conductivity[16] indicate that phonons are scattered in this alloy predominantly through the mass-defect mechanism, a conclusion supported by the results of the current investigation. The Cu-Ag results indicate that, in this alloy, the contribution from lattice distortion is predominant. In this respect, it is of interest to compare the results for the gold and silver alloys. The wide range of solid solubility for gold in copper[17] indicates that, in this alloy, the solute atoms should not unduly disturb the host lattice. Hence one should be able to calculate the phonon-scattering probability reasonably well by considering only mass difference. On the other hand, the solubility of silver in copper is rather limited,[17] while the $(\Delta M/M)^2$ term is much less than that for copper-gold. From these considerations, in agreement with the present results, a much larger relative contribution would be expected from lattice distortion in Cu-Ag as compared to Cu-Au.

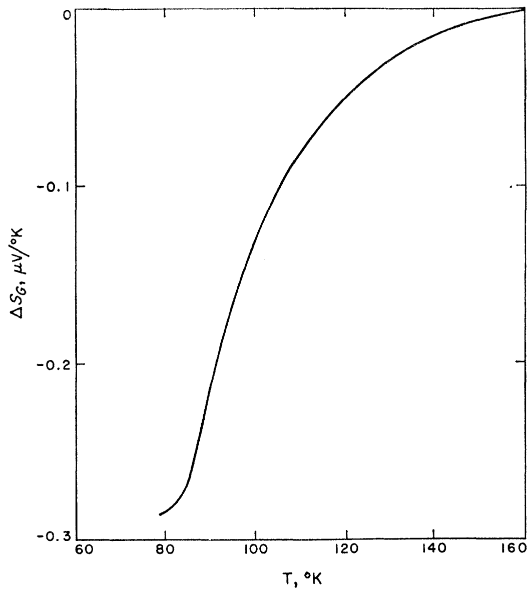

FIG. 5. ΔS_g, the difference in phonon drag thermopower between Cu+0.44% Si and pure copper.

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