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Deviation from Matthiessen's rule at high temperatures: Theoretical interpretation

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Theoretical interpretation is given for the deviation from Matthiessen's rule (DMR) at high temperatures on dilute alloy systems Au in Cu, Cu in Au, and Ni in Cu, and Cu, Ag, and Ge in Al, measured with the use of the new experimental techniques developed by Fujita and others. The measured deviation from this rule, $\Delta(c,T)$, can be fitted to curves of $Y+AT$ ($Y\approx 0$), where T is the absolute temperature, and the numerical constant A (Y) can be calculated using a standard lowest-order (higher-order) variational scheme. Y is always positive and gives a measure of the anisotropy of the scattering at high temperatures. For most of the Al-based and noble-metal-based dilute alloys, Y is small and the anisotropy scattering is unimportant. The proportionality factor A has been evaluated, within the standard variational formalism, using an atomistic model calculation for the electron-phonon spectral function. It is shown that the leading contribution to the high-temperature DMR is due to the change in the phonon spectral function $F(\omega)$ for Cu in Al, Ge in Al, Cu in Au, and Au in Cu alloys, while it comes from the change in the electron-phonon coupling function $\alpha_{\text{tr}}^2(\omega)$ (electron-mass-enhancement parameter λ_{tr}) for the Ag in Al alloy.

I. INTRODUCTION

The general feature of the deviation from Matthiessen's rule (DMR) at high temperatures close to the melting point was obtained for dilute Al-based alloys, Cu, Ag, and Ge in Al, with the use of an impurity-diffusion technique by Fujita *et al.*,[1] and quite recently DMR results for noble-metal-based alloys, Au in Cu, Cu in Au, and Ni in Cu, have been obtained as well.[2]

This paper provides theoretical interpretation for these DMR results. There have been a number of theoretical approaches on DMR in dilute alloys as well as metals containing lattice imperfections.[3,4] Sondheimer and Wilson[5] introduced a two-band model of electronic conduction and demonstrated that DMR appears owing to anisotropy of relaxation time in each band (belly and neck region of Fermi surface). Kohler,[6] on the other hand, introduced the variational procedure for solving the Boltzmann transport equation, which has been used to determine DMR $\Delta(c,T)$ (for definition see Sec. II) arising from the inelastic electron scattering by phonons.[7] Kagan and Zhernov,[8] Taylor, Kus *et al.*,[9] and others have discussed the Debye-Waller factor in the electron-phonon scattering. Goodarz and Barnard[10] considered the influence of a rapidly varying electron density of states as a function of energy at the Fermi level.

Theories proposed so far, however, seem to be unsatisfactory at high temperatures near the melting point, since assumptions introduced may be only valid at low and intermediate temperatures.[3,8] In the present paper we propose, on the basis of experimental findings on high-temperature DMR obtained by Fujita *et al.*[1,2] using a specifically designed impurity-diffusion technique, a straightforward and transparent mechanism for DMR of dilute binary alloys at high temperatures. The idea is similar to that proposed by Berry[11] and that proposed recently by Engquist and Grimvall.[12] We propose that at high temperatures the change in the electron-phonon spectral function $\alpha_{\mathrm{tr}}^2(\omega)F(\omega)$ due to solute atoms (or defects) plays a dominant role in determining DMR, and other effects such as anisotropic electron scattering, energy dependence of relaxation time, etc., are of secondary importance. In fact, as shown by Engquist and Grimvall,[12] $\Delta(c,T)$ arising from the anisotropic scattering becomes very small at high temperatures above 300 K.

We investigate the change in the $F(\omega)$ and $\alpha_{\mathrm{tr}}^2(\omega)$ functions as follows: To estimate the change in phonon spectral function $F(\omega)$ upon alloying, we use the Debye model and moment (Thirring) expansion technique.[13] Furthermore, for the estimation of the change in the electron-phonon coupling function $\alpha_{\mathrm{tr}}^2(\omega)$, we assume (see Ref. 14)

$$\alpha_{\mathrm{tr}}^2(\omega)F(\omega)\propto\lambda_{\mathrm{tr}}(\omega/\omega_D)^4$$

and use a simple interpolation scheme for the coupling constant λ_{tr} (electron-mass-enhancement parameter) of dilute alloys,[15] i.e.,

$$\frac{d\lambda_{\mathrm{tr}}}{dc}\approx\frac{\lambda_{\mathrm{tr}}}{(d\rho/dT)}\left[\frac{d^2\rho}{dTdc}\right]$$

or[16,17]

$$\lambda_{\mathrm{tr}}^{\mathrm{alloy}}=C_A\lambda_{\mathrm{tr}}^A+(1-C_A)\lambda_{\mathrm{tr}}^B\ ,$$

together with the well-known relation[18]

$$\lambda_{\mathrm{tr}}=2\int_0^\infty\frac{d\omega}{\omega}\alpha_{\mathrm{tr}}^2(\omega)F(\omega)\ , \tag{1}$$

where ρ denotes the resistivity of the alloy. This assumption has widely been used in the literature (DMR theory at low and intermediate temperatures[12] and calculation of infrared absorption in metals[18]) with considerable success. Thus it can also be used for the semiquantitative understanding of high-temperature DMR. To characterize the change in the phonon spectral function $F(\omega)$, we determine the change in the characteristic (Debye) temperature $\Delta\Theta_D$ upon alloying. We derive an analytical expression for $\Delta\Theta_D$ and give numerical estimates of $\Delta\Theta_D$ for specific alloy systems. To our knowledge, this is the first time that DMR $\Delta(c,T)$ has been calculated using an atomistic model of lattice vibration for binary alloys at high temperatures, and compared directly with the specific experimental systems. So far, theories for DMR have been concerned in the main with low and intermediate temperatures, where the characteristic hump (or peak) appears and DMR becomes a maximum.[19] As will be shown later, the present theoretical calculations of DMR at high temperatures are in good agreement with experimental results.

The present paper is organized as follows: In Sec. II we present the method of calculation. Section III contains the numerical results and discussions for high-temperature DMR of dilute binary (Al-based as well as noble-metal-based) alloys. The conclusions are given in Sec. IV.

II. METHOD OF CALCULATION

The DMR arises from the simultaneous presence of electron-impurity (lattice-defect) scattering and of electron-phonon scattering. We denote by $\rho_0(c)$ the residual resistivity arising from electron-impurity scattering in the absence of electron-phonon scattering, and by $\rho_p(T)$ the ideal resistivity arising from electron-phonon scattering in the absence of electron-impurity scattering. The DMR $\Delta(c,T)$ is then defined as

$$\Delta(c,T)=\rho(c,T)-\rho_p(T)-\rho_0(c)\ , \tag{2}$$

where $\rho(c,T)$ denotes the resistivity of the alloy with solute concentration c. The major part of the DMR problem is thus how to calculate the resistivity $\rho(c,T)$ at finite temperatures.

Semiquantitative understanding of DMR at low and intermediate temperatures have been given in the literature[12,19] but at high temperatures theoretical interpretation has not been given yet. One of the reasons is the fact that there has been no reliable experimental data of DMR at high temperatures. Another reason is the difficulty of exactly solving the problem, for instance, the difficulty of taking into account the multiphonon and other processes. However, in view of the experimental results of DMR at high temperatures, where linear temperature dependence is obtained for a wide variety of binary alloy systems (except for the Ni*Cu* alloy, for instance)[1,2] we may expect that DMR at high temperatures can be treated within the standard variational formalism.[18,20,21] It is exactly what we attempt to do in this paper.

We introduce the so-called "electron-phonon spectral function" in the theory of DMR. It is very convenient to introduce the electron-phonon spectral function (so-called Eliashberg function) $\alpha_{tr}^2(\omega)F(\omega)$ in the transport theory because, in the absence of detailed knowledge, we can still make good guesses about $\alpha_{tr}^2(\omega)F(\omega)$. Using the standard variational formalism,[18,20,21] the DMR of dilute binary alloys can be written formally as

$$\begin{aligned}\Delta(c,T)&=[\rho(c,T)-\rho_p(c,T)-\rho_0(c)]+[\rho_p(c,T)-\rho_p(T)]\\&=[\rho(c,T)-\rho_p(c,T)-\rho_0(c)]+\frac{4\pi m^*}{ne^2}\int_0^\infty\frac{\{[\alpha_{tr}^2(\omega)F(\omega)]^c-[\alpha_{tr}^2(\omega)F(\omega)]^0\}}{(e^{\beta\omega}-1)(1-e^{-\beta\omega})}\beta\omega\,d\omega\,,\end{aligned}\tag{3}$$

where $\beta=1/k_BT$, and m^*, e, and n denote electron mass, electronic charge, and electron density, respectively.

To investigate the first term of the above equation (3) (which becomes important at low and intermediate temperatures), Engquist and Grimvall[12] have solved the Fredholm-type integral equation and obtained the energy-dependent relaxation time. They showed that the model calculations are not sensitive to details in the $\alpha_{tr}^2(\omega)F(\omega)$ function and the quantity in the first bracket can be approximated by that for $c=0$. At high temperatures and at low concentrations c, Eq. (3) can be simplified to

$$\Delta(c,T)=Y+AT\,.\tag{4}$$

From Eq. (4), one can summarize the theoretical predictions as follows: A plot of measured $\Delta(c,T)/\rho_0(c)$ for dilute alloys, as a function of temperature, has one of the two typical forms sketched in Fig. 1. The factor Y is always positive and gives a measure of the anisotropy of the scattering at high temperatures.[12] A can be calculated only if we know the details of how $\alpha_{tr}^2(\omega)F(\omega)$ is changed on alloying. In general, it is difficult to obtain this kind of information. In the present study, we use a rather simple scheme to obtain the change in the $\alpha_{tr}^2(\omega)F(\omega)$ function. We use the Debye model for the phonon spectral function $F(\omega)$ and the relation between the coupling constant λ_{tr} and $\alpha_{tr}^2(\omega)F(\omega)$ function, given in Eq. (1). The value of $\lambda_{tr}^{\text{alloy}}$ is estimated using the simple interpolation scheme[15]:

$$\frac{d\lambda_{tr}}{dc}\approx\frac{\lambda_{tr}}{(d\rho/dT)}\left[\frac{d^2\rho}{dT\,dc}\right]$$

and[16,17]

$$\lambda_{tr}^{\text{alloy}}=C_A\lambda_{tr}^A+(1-C_A)\lambda_{tr}^B\,.$$

The change in the phonon spectral function $F(\omega)$ due to solute atoms is investigated using the moment (Thirring) expansion technique.[13]

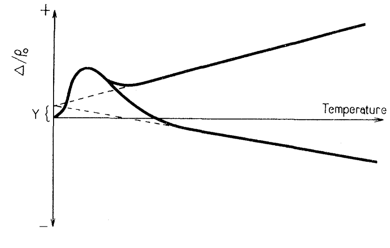

FIG. 1. Typical experimental DMR curves in the entire temperature region.

A. Change in the characteristic temperature

In this section we derive the formula to evaluate the change in the characteristic temperature due to solute atoms and apply it to DMR calculations. In order to calculate the characteristic (Debye) temperature of dilute alloys or metals with lattice imperfections, $\Theta_D=\Theta_0+\Delta\Theta_D$, we use the well-known relation[13] between the second frequency moment μ_2 of a frequency (Debye) spectrum and the characteristic (Debye) temperature,

$$\mu_2=\frac{3}{5}\left[\frac{k_B}{\hbar}\Theta_D\right]^2\,.\tag{5}$$

From Eq. (5), it is straightforward to derive

$$\delta\Theta_D=\frac{\hbar}{k_B}\left[\frac{5}{12}\right]^{1/2}\frac{\delta\mu_2}{(\mu_2^{(0)})^{1/2}}\,.\tag{6}$$

Rigorously speaking, $\delta\Theta_D$ should be calculated including the temperature dependence of the characteristic temperature Θ_D, and be expressed in terms of the change in the frequency moments $\delta\mu_2$, $\delta\mu_4,\ldots,\delta\mu_n,\ldots,$ and temperature T (see Appendix A).

In order to obtain the change in the nth moment $\delta\mu_n$, due to the introduction of solute atoms, it is convenient to introduce the dynamical matrix $D_{\alpha\beta}$ and use the following formula[13]:

$$\mu_{2n}=\int_0^{\omega_{\max}}\omega^{2n}F(\omega)d\omega=\frac{1}{3N}\,\mathrm{Tr}D^n_{\alpha\beta}\ . \tag{7}$$

After a bit of algebra, one obtains, for instance, $\Delta\mu_2$ for the fcc lattice with the nearest-neighbor interaction as follows:

$$\Delta\mu_2=\mu_2-\mu_2^{(0)}$$
$$=\frac{4}{N}\left[\left[\frac{1}{M}+\frac{1}{M'}\right]\lambda_{hi}(R_0')-\frac{2}{M}\lambda_{hh}(R_0)\right]\ , \tag{8}$$

where M and M' denote the host and impurity masses, respectively. $\lambda_{hh}(R_0)$ represents the force constant between host atoms separated by an equilibrium interatomic distance R_0, and $\lambda_{hi}(R_0')$ between host and impurity atoms separated by a distance R_0' (due to lattice distortion around the impurity atom). $\lambda_{hh}(R_0)$ can, in principle, be determined from the bulk maximum frequency $\omega_{\max}$. In contrast, the determination of host-impurity force constants $\lambda_{hi}(R_0')$ is difficult and will be made using a phenomenological pair potential method.

B. Host-impurity interaction energy

In general, it is difficult to obtain the force constants between host and impurity atoms since they depend both on the changes in the electronic structure and short-range ion-core interactions due to introduction of solute atoms. Mössbauer spectroscopy or neutron diffraction experiments can give, to some extent, information on this quantity.[22,23] However, these kinds of experiments have been very limited (for instance, limited to Mössbauer impurities such as Sn and Fe, and neutron experiments have been done for rather concentrated alloys with a few at.% of solutes or more) and no reliable experimental data are available for the Al-based and noble-metal-based alloys considered here (very dilute). The pseudopotential or density-functional approach[24,25] may be applicable to this kind of problem but at present very reliable results could not be expected from these calculations.

We evaluate the host-impurity force constants (interactions) from the theoretical calculations using a simple pair potential method recently introduced and applied to a wide variety of metals and alloys with considerable success.[26,27] This method is based on a rather simple but transparent rule called a combination rule, and gives in a straightforward fashion the pair interaction between host and impurity atoms.

The Morse potentials

$$\phi_\gamma(R_{ij})=D_\gamma\{\exp[-2\alpha_\gamma(R_{ij}-R_{0\gamma})]-2\exp[-\alpha_\gamma(R_{ij}-R_{0\gamma})]\}\ ,\quad \gamma=A\ \text{or}\ B\ , \tag{9}$$

fitted to the bulk modulus, lattice constant, and the cohesive energy (or a formation energy of a vacancy) are used to describe interactions between atoms in pure A or B metals and

$$\chi(R_{ij})=\tilde{D}\{\exp[-2\tilde{\alpha}(R_{ij}-\tilde{R}_0)]-2\exp[-\tilde{\alpha}(R_{ij}-\tilde{R}_0)]\}\ , \tag{10}$$

are used for the interaction between host and impurity atoms. The potential parameters $\tilde{D}$, $\tilde{\alpha}$, and $\tilde{R}_0$ are determined from parameters D_A, α_A, R_{0A}, D_B, α_B, and R_{0B} for constituent A and B pure metals using a combination rule.

Once potential functions for A-B atom interactions are known, it is straightforward to determine the change in the first few moments $\delta\mu_n$ due to introduction of solute atoms. For instance, in terms of the first and second derivatives of the potential functions ϕ and χ and host and impurity masses M and M', $\delta\mu_2$ can be expressed as

$$\delta\mu_2=\frac{4}{N}\left[\left[\frac{1}{M}+\frac{1}{M'}\right]\left[\chi''(R_0)+\frac{2}{R_0}\chi'(R_0)\right]-\frac{2}{M}\phi''(R_0)\right]\ . \tag{11}$$

The detailed derivation of the above equation will be presented in the Appendix. It is then straightforward to evaluate the change in the characteristic temperature $\Delta\Theta$ due to introduction of solute atoms from Eq. (6).

III. NUMERICAL RESULTS AND DISCUSSIONS

In this section we present the results of numerical calculations of high-temperature DMR $\Delta(c,T)$

for both Al-based and noble-metal-based binary alloys and compare them with experimental data obtained using the new experimental (impurity diffusion) techniques developed by Fujita *et al.*[1,2] For convenience, we calculate $\Delta(c,T)/\rho_p(T)$ as a function of atomic concentration of solute atoms c. We assume that the change in the characteristic temperature Θ due to introduction of solute atoms is identical to the change in the Debye temperature, obtained for instance from Eq. (6).

The parameter values of Morse potential D, α, and R_0 are now well known for a wide variety of metals.[26,27] With the use of these values it is possible to calculate the cohesive energy E_c, bulk maximum frequency $\omega_{\max}$, and Debye temperature Θ_D (both for the host metals as well as for metals composed only of solute elements). In order to investigate the $\Delta(c,T)$ arising from the change in the electron-phonon spectral function $\alpha_{\text{tr}}^2(\omega)F(\omega)$ upon alloying (at high temperatures), we first calculate $\Delta(c,T)$ taking into account the change in the phonon spectral function $F(\omega)$, i.e., change in Θ_D due to the introduction of solute atoms, and leaving the other factors unchanged. Second, we calculate $\Delta(c,T)$ taking into account the change in the electron-phonon coupling function $\alpha_{\text{tr}}^2(\omega)$: In the present work using the Debye model and assuming[14] that

$$\alpha_{\text{tr}}^2(\omega)F(\omega)\propto\lambda_{\text{tr}}(\omega/\omega_D)^4 \ ,$$

the change in ω_D or Θ_D affects both $F(\omega)$ and $\alpha_{\text{tr}}^2(\omega)$ functions simultaneously. However, in order to avoid confusion, the change in the $\alpha_{\text{tr}}^2(\omega)$ function is hereafter referred to as the change in the coupling constant λ_{tr}. From these calculations we understand the leading contribution to the DMR function $\Delta(c,T)$.

Introduction of solute atoms or lattice defects can change the Debye temperature of the crystal. This behavior has been investigated both experimentally and theoretically. For example, measurements of the lattice specific heat and the elastic constants both show that the Debye temperature Θ_D (at 0 K) may change linearly with dilute solute concentration.[28] It has also been demonstrated that the increase in specific heat in the temperature range between $\frac{1}{10}\Theta_D$ and Θ_D, caused by plastic deformation, can be approximately represented within the Debye theory.[29] It is, therefore, reasonable to assume that the phonon resistivity is altered to some extent by solute atoms or defects and that this change could be represented by a change in the characteristic temperatures.

We have calculated the change in the characteristic temperature $\Delta\Theta_D$ due to introduction of 0.1 at. % solute atoms and presented the results in Table I. One can see that $\Delta\Theta_D$ becomes positive or negative depending on the mass ratio M'/M and the host-impurity force constants. Once the change in the characteristic temperature $\Delta\Theta_D$ is calculated, it is straightforward to obtain $\Delta(c,T)$. In this case ($\Delta\Theta_D$ model), the DMR $\Delta(c,T)$ can be expressed in terms of $\Delta\Theta_D$ as follows[11]:

$$\Delta(c,T)\approx Y-2\frac{\Delta\Theta_D}{\Theta_D}\rho_p(T) \ . \tag{12}$$

In Figs. 2 and 3 we present $\Delta(c,T)/\rho_p(T)$ for alloy systems Cu in Al and Ge in Al, respectively, assuming the change in the phonon spectral function $F(\omega)$ only. Experimental results are represented by symbols ○. The corresponding results for Au in Cu and Cu in Au are given in Figs. 4 and 5, respectively. In general, the agreement between theory and experiment is good: Even for the results of Cu in Au shown in Fig. 5, the agreement in sign and in order of magnitude is of significance, in view of the rough estimation for the $\alpha_{\text{tr}}^2(\omega)F(\omega)$ function. Here, it is noted that experimental $\Delta(c,T)$ data can be fitted well to curves with $Y\approx 0$. This indicates that the DMR $\Delta(c,T)$

TABLE I. Calculated λ_0'/λ_0 and $\Delta\Theta$. $\Delta\Theta$ is evaluated for 0.1 at % alloys. $\Delta\Theta^*$ is obtained assuming $\lambda_0'/\lambda_0=1$ (M'/M is taken into account).

Host	Impurity	M'/M	λ_0'/λ_0	$\Delta\Theta^*\times 10^{-1}$ (K)	$\Delta\Theta\times 10^{-1}$ (K)
Al	Cu	2.355	1.302	−1.235	−0.318
Al	Ag	3.998	1.283	−1.610	−0.852
Al	Ge	2.691		−1.349	
Cu	Ni	0.9237	1.137	0.435	0.693
Cu	Au	3.1004	1.202	−1.279	−0.775
Au	Cu	0.3225	0.841	2.059	1.855

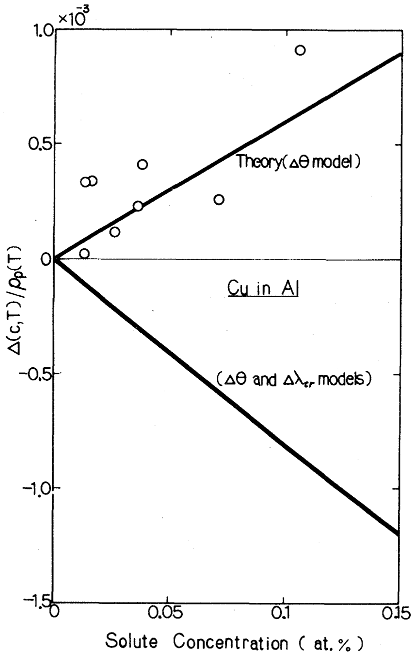

FIG. 2. Comparison of experimental data with theory for Cu in Al alloy system.

for binary alloys at high temperatures may be largely accounted for by a change in the characteristic temperature alone. Furthermore, it is important that these conclusions are not altered qualitatively even when we take into account the change in the electron-phonon coupling function $\alpha_{tr}^2(\omega)$ simultaneously, as will be shown later. The exception is for Cu in Al alloys. This might indicate that the estimation of the $\Delta\lambda_{tr}$ value using the simple interpretation schemes is inappropriate for the alloys. In this respect it is desirable to establish an *ab initio* theoretical method to calculate the $\Delta\lambda_{tr}$ values.

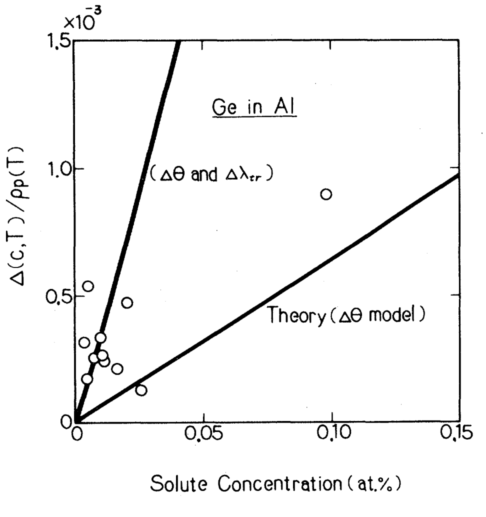

FIG. 3. Comparison of experimental data with theory for Ge in Al alloy system.

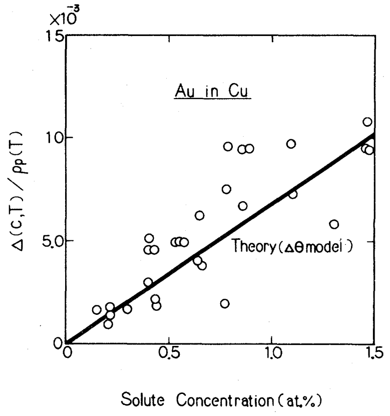

FIG. 4. Comparison of experimental data with theory for Au in Cu alloy system.

Furthermore, theoretical prediction that the sign of DMR $\Delta(c,T)$ is opposite to that of $\Delta\Theta_D$ [Eq. (18)] is in agreement with our experimental findings.[1,2] It is noted that the experimental values of $\Delta(c,T)/\rho_p(T)$ for Au in Cu have a positive sign, while those for Cu in Au a negative sign. This also indicates the positive identification of the $\Delta\Theta_D$ model for the DMR at high temperatures. [Historically, there have been several attempts[11,29,30] to interpret the experimental data in terms of the change in the characteristic temperature ($\Delta\Theta_D$ model). However, these attempts do not seem to have succeeded since they have too many unknown factors[11] and many experimental results reported for very dilute alloys are unphysical at high temperatures (they do not approach an asymptotic curve when impurity concentration c tends to zero[12]).] In contrast to the alloy systems Cu in Al, Ge in Al, Au in Cu, and Cu in Au, the agreement between the $\Delta\Theta_D$ model calculation and experiments is poor for Ag in Al and Ni in Cu. The $\Delta\Theta_D$ model predicts the opposite sign, compared to experimental results, for $\Delta(c,T)/\rho_p(T)$ of these alloys. This probably comes from the fact that the $\alpha_{tr}^2(\omega)$ function is altered upon alloying as well. It is well known that not only $F(\omega)$ but also $\alpha_{tr}^2(\omega)$ functions change upon alloying, especially in the experience of superconducting materials.[17] We now estimate the contribution of $\Delta(c,T)$ coming from the change in the electron-phonon coupling function $\alpha_{tr}^2(\omega)$, i.e., the change in the coupling

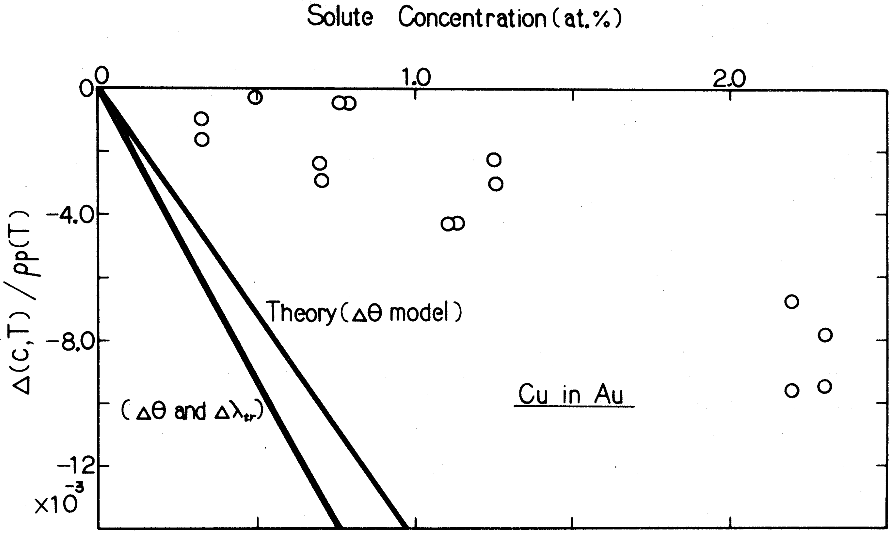

FIG. 5. Comparison of experimental data with theory for Cu in Au alloy system.

constant λ_{tr}. For this purpose, we assume[18] that

$$\alpha_{tr}^2(\omega)F(\omega)=2\lambda_{tr}(\omega/\omega_D)^4$$

both for pure metals and dilute binary alloys. This form of the electron-phonon spectral function $\alpha_{tr}^2(\omega)F(\omega)$ directly reproduces the Bloch-Grüneisen resistivity formula[20] for the pure metals. Now it is possible to obtain the DMR arising from the change in the coupling constant λ_{tr}:

$$\Delta(c,T)\approx Y+\frac{4\pi m^*}{ne^2}\frac{2\Delta\lambda_{tr}}{\beta^5\omega_D^4}F(\hbar\omega_D/k_BT)\ , \tag{13}$$

where

$$F(x)=\int_0^x \frac{Z^5}{(e^Z-1)(1-e^{-Z})}dZ\ ,$$
$$\Delta\lambda_{tr}=\lambda_{tr}^{\text{alloy}}-\lambda_{tr}^{\text{pure}}\ . \tag{14}$$

We now evaluate $\Delta(c,T)/\rho_p(T)$ using Eqs. (13) and (14), and assuming

$$d\lambda_{tr}/dc\approx[\lambda_{tr}/(d\rho/dT)](d^2\rho/dT\,dc)$$

or

$$\lambda_{tr}^{\text{alloy}}=(1-C)\lambda_{tr}^A+C\lambda_{tr}^B$$

for comparison. The second approximation is exact in the weak scattering limit.[31] The first type of approximation for $(d\lambda/dc)$ has been used by Rapp *et al.*[15] and Grimvall[32] for a large number of alloys with considerable success. [Both approximations give almost the same results (tendency) for the alloy systems considered here.]

The calculated $\Delta\lambda_{tr}$ values are presented in Table II for Al-based and noble-metal-based binary alloys, together with λ_{tr} values (in parenthesis) for the pure constituent metals. From Table II one can see that $\Delta\lambda_{tr}$ contribution to the DMR is most important for Ag in Al while it is less important for Cu in Al, Cu in Au, and Au in Cu alloy systems. In Fig. 5, we present $\Delta(c,T)/\rho_p(T)$ for Ag in Al: Symbols ○ represent the experimental data. One can see that the agreement between the theory and experiment is good. For Ag in Al, better agreement is obtained when including both changes in Θ_D and λ_{tr}. In view of the simple assumption for values of $\lambda_{tr}^{\text{alloy}}$, the present success of the DMR $\Delta(c,T)$ calculation is encouraging: In an exploratory model calculation, the simplicity of the assumption or transparency of a theory is quite desirable for the semiquantitative understanding of the problem (complicated DMR mechanism at high temperatures). From these calculations, we come to the conclusion that the DMR of binary alloys considered here can roughly be accounted for within the standard variational formalism.[20] For Cu in Al, Ge in Al, Cu in Au, and Au in Cu alloy systems, the leading contribution to the DMR can be explained by the $\Delta\Theta_D$ model while the $\Delta\lambda_{tr}$ mechanism can be applied to Ag in the Al system (better agreement is obtained by including both

TABLE II. Calculated $\Delta\lambda_{tr}/\lambda_{tr}$ using the interpolation schemes for 0.1 at % alloys.

Host	Impurity	$\Delta\lambda_{tr}/\lambda_{tr}$[a] (interpolation)	$\Delta\lambda_{tr}/\lambda_{tr}$[b]
Al (0.49)	Ag (0.10)	-0.8×10^{-3}	-3.1×10^{-3}
Al (0.49)	Cu (0.14)	-0.7×10^{-3}	-1.4×10^{-3}
Cu (0.14)	Au (0.14)	0	0
Au (0.14)	Cu (0.14)	0	-0.4×10^{-3}
Al (0.49)	Ge		$+3.0\times10^{-3}$

[a] These values are obtained from the relation $\lambda_{tr}^{alloy}=C_A\lambda_{tr}^{A}+C_B\lambda_{tr}^{B}$.

[b] These values are obtained from the interpolation schemes given by Rapp and Fogelholm (Ref. 15) and the experimental data by Fujita *et al.* (Ref. 1). We have used these values in the present DMR calculations since they are obtained by taking into account the characteristic features of the resistivity of very dilute alloys.

$\Delta\lambda_{tr}$ and $\Delta\Theta_D$ contributions as shown in Fig. 6).

However, the agreement between the present DMR calculation and experimental results is poor for the Ni*Cu* alloy system, where nonlinear temperature dependence of $\Delta(c,T)$ has been observed at temperatures 295—1163 K. This might come from the fact that in dilute Ni*Cu* alloys other mechanisms like *sp* electron scatterings from *d* resonance states play a significant role even at high temperatures.

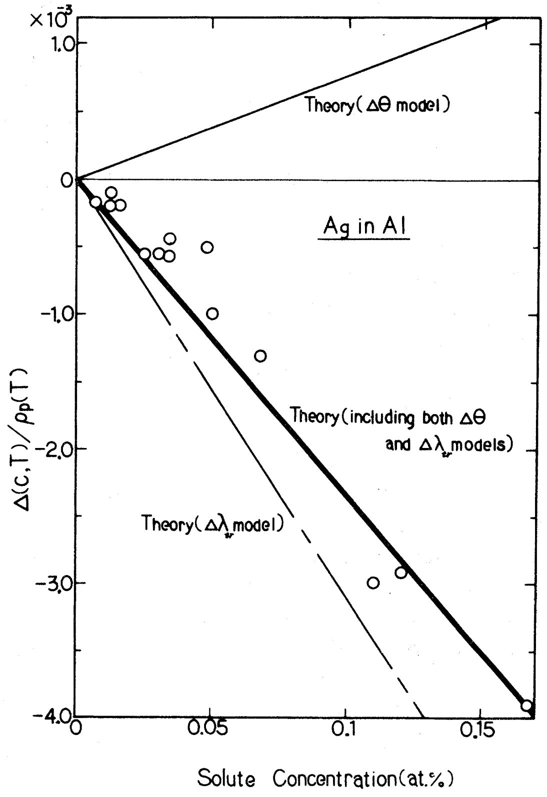

FIG. 6. Comparison of experimental data with theory for Ag in Al alloy system. Solid (dot-dashed) curve represents theoretical results from $\Delta\Theta_D(\Delta\lambda_{tr})$ model. Bold solid curve is obtained by including both $\Delta\Theta_D$ and $\Delta\lambda_{tr}$ contributions.

IV. CONCLUSIONS

Theoretical interpretation for high-temperature DMR has been given for Al-based and noble-metal-based alloys using an atomistic lattice-vibration calculation within the standard variational formalism. For most of the binary alloys, the experimental DMR $\Delta(c,T)$ data can be fitted well to curves of $Y+AT$ $(Y\approx0)$. This indicates that the anisotropic scattering owing to impurity atoms is unimportant at high temperatures. We have also shown that the leading contribution to the DMR is owing to the change in the phonon spectral function $F(\omega)$, i.e., change in Debye temperature, for alloy systems of Cu in Al, Ge in Al, Cu in Au, and Au in Cu, while it comes from the change in the electron-phonon coupling function $\alpha_{tr}^2(\omega)$ (the coupling constant λ_{tr}) for Ag in the Al alloy system. These contributions have not been included in the previous DMR theories such as the two-band theory, Kagan and Zhernov theory, and others (appropriate for low and intermediate temperatures).

However, the other mechanisms like *s-d* or *p-d* scatterings have to be added for Ni*Cu* alloy, which show the nonlinear temperature dependence of $\Delta(c,T)$ at high temperatures. Though the present calculation does not give detailed quantitative understanding for the high-temperature DMR of binary alloy systems, it does provide a general physical interpretation for the high-temperature DMR: The $\Delta\Theta_D$ and $\Delta\lambda_{\mathrm{tr}}$ mechanisms have not been included in the previous low-temperature DMR calculations. For more quantitative understanding it is required at least to introduce the more realistic phonon spectra or electron-phonon spectral functions. Such attempts have already been made for the resistivity calculation of pure metals.[33] We hope that the present theoretical interpretations and discussions will stimulate more theoretical and experimental works on the DMR at high temperatures.

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APPENDIX A

The explicit expression for the characteristic temperature Θ_D can be given as follows: We start with the relation between the specific heat of the crystal (constant volume) and the vibrational spectrum $F_D(\omega)$,

$$C_v(T)=\frac{\partial E_{\mathrm{tot}}}{\partial T}=3Nk_B\int_0^\infty \frac{x^2}{\sinh^2 x}F_D(\omega)d\omega$$
$$+3N\frac{\partial\omega_D}{\partial T}\frac{\partial}{\partial\omega_D}\int_0^\infty\left[\frac{\hbar\omega}{2}+\frac{\hbar\omega}{e^{\hbar\omega/k_BT}-1}\right]F_D(\omega)d\omega\ . \qquad \text{(A1)}$$

The second term of Eq. (A1) arises from the temperature dependence of ω_D. This term can be shown to be negligible since it has T^{-4}, T^{-6}, . . . contributions (without T^{-2} contribution). Then it is easy to derive

$$\Theta_D=\left[\frac{\hbar}{k_B}\right]\left[\frac{5}{3}\mu_2^{(0)}+\frac{5}{3}\delta\mu_2\right]^{1/2}$$
$$+\frac{1}{T^2}\frac{1}{8}\left[\frac{\hbar}{k_B}\right]^3\left[\frac{1}{7}\left[\frac{5}{3}\right]^{3/2}\left[\mu_2^{(0)}+\delta\mu_2\right]^{3/2}-\frac{1}{3}\left[\frac{3}{5}\right]^{1/2}\frac{\mu_4^{(0)}+\delta\mu_4}{(\mu_2^{(0)}+\delta\mu_2)^{1/2}}\right]+O(T^{-4})\ , \qquad \text{(A2)}$$

where we have used the Thirring expansion technique and assumed that

$$\Theta_D=\Theta_D^\infty+\frac{C_2}{T^2}+\frac{C_4}{T^4}+\frac{C_6}{T^6}+\cdots\ . \qquad \text{(A3)}$$

Here C_{2n} denotes numerical constants. From Eq. (A2) one can see that $\delta\Theta_D$ can be well approximated by the expression (6) at high temperatures.

APPENDIX B

In this appendix we derive Eq. (11) in the text within the central-force harmonic approximation. When the host-atom site, origin of a host lattice, is replaced by an impurity atom, the total potential energy V of the crystal can be written as

$$V=\tfrac{1}{2}\sum_{l}\sum_{l'\neq 0}\phi(\,|\vec{r}_l-\vec{r}_{l'}|\,)$$
$$+\sum_{l\neq 0}[X(\,|\vec{r}_l-\vec{r}_0|\,)-\phi(\,|\vec{r}_l-\vec{r}_0|\,)],$$
$$\equiv\Phi+\Delta\Phi\ , \qquad \text{(B1)}$$

where $\phi(\,|\vec{r}_l-\vec{r}_{l'}|\,)$ and $X(\,|\vec{r}_l-\vec{r}_{l'}|\,)$ are the pair interaction energies between pairs of host atoms and between host and impurity atoms separated by a distance $|\vec{r}_l-\vec{r}_{l'}|$, respectively. We denote the lattice vector $\vec{r}_l$ in terms of the equilibrium position $\vec{x}_l$, and displacement vector $\vec{\xi}_l$ as

$$\vec{r}_l=\vec{X}(l)+\vec{\xi}(l)\ . \qquad \text{(B2)}$$

We now expand the potential energy in powers of ξ:

$$\Phi=\Phi_0+\tfrac{1}{2}\sum_{l\alpha}\sum_{l'\beta}\Phi^{(0)}_{\alpha\beta}(ll')\xi_\alpha(l)\xi_\beta(l')+\cdots\ , \tag{B3}$$

$$\begin{aligned}\Delta\Phi=\Delta\Phi_0&+\sum_{l\neq 0,\alpha}\rho_\alpha(l)[\xi_\alpha(l)-\xi_\alpha(0)]\\&+\tfrac{1}{2}\sum_{l\neq 0}\sum_{\alpha\beta}\rho_{\alpha\beta}(l)[\xi_\alpha(l)-\xi_\alpha(0)]\\&\times[\xi_\beta(l)-\xi_\beta(0)]+\cdots\ ,\end{aligned} \tag{B4}$$

where $\xi_\alpha(l)$ is the α Cartesian component of $\vec{\xi}(l)$ and $\rho(r)=\chi(r)-\phi(r)$. Furthermore, in the above equations (B3) and (B4), we have used the notation

$$\Phi_0=\tfrac{1}{2}\sum_{l\neq l'}\phi(\,|\,\vec{x}(l)-\vec{x}(l')\,|\,)\ , \tag{B5}$$

$$\begin{aligned}\Phi^{(0)}_{\alpha\beta}(l,0)=\Phi^{(0)}_{\alpha\beta}(0,l)&=-\phi_{\alpha\beta}(l)\\&=-[\chi_\alpha(l)\chi_\beta(l)D^2\phi(l)\\&\quad+\delta_{\alpha\beta}D\phi(l)],\ \ l\neq 0\end{aligned} \tag{B6}$$

$$\Phi^{(0)}_{\alpha\beta}(0,0)=\sum_{l\neq 0}\phi_{\alpha\beta}(l)\ , \tag{B7}$$

and

$$\Delta\Phi_0=\sum_{l}\rho(\,|\,\vec{\chi}(l)\,|\,)\ , \tag{B8}$$

$$\begin{aligned}\rho_\alpha(l)&=\frac{\partial}{\partial\chi_\alpha}\rho(r)\bigg|_{r=\chi(l)}\\&=\chi_\alpha(l)D\rho(l)\ ,\end{aligned} \tag{B9}$$

$$\begin{aligned}\rho_{\alpha\beta}(l)&=\frac{\partial^2}{\partial\chi_\alpha\partial\chi_\beta}\rho(r)\bigg|_{r=\chi(l)}\\&=\chi_\alpha(l)\chi_\beta(l)D^2\rho(l)\ +\delta_{\alpha\beta}D\rho(l)\ ,\end{aligned} \tag{B10}$$

where D represents the differential operator.

One can rewrite Eq. (B4) as

$$\begin{aligned}\Delta\Phi=\Delta\Phi_0&+\sum_{l,\alpha}f_\alpha(l)\xi_\alpha(l)\\&+\tfrac{1}{2}\sum_{l\alpha}\sum_{l'\beta}f_{\alpha\beta}(l,l')\xi_\alpha(l)\xi_\beta(l')+\cdots\ ,\end{aligned} \tag{B11}$$

$$f_\alpha(l)=\rho_\alpha(l),\ \ l\neq 0 \tag{B12}$$

$$=-\sum_{l\neq 0}\rho_\alpha(l)\ . \tag{B13}$$

We now write the displacement vector $\vec{\xi}(l)$ as the summation of a static displacement $\vec{v}(l)$ and of a dynamic displacement $\vec{u}(l)$. The potential energy can be expanded as

$$\begin{aligned}\bar{V}=\Phi_0+\Delta\Phi_0&+\sum_{l\alpha}f_\alpha(l)v_\alpha(l)+\tfrac{1}{2}\sum_{l\alpha}\sum_{l'\beta}[\Phi^{(0)}_{\alpha\beta}(l,l')+f_{\alpha\beta}(l,l')]v_\alpha(l)v_\beta(l')+\cdots\\&+\sum_{l\alpha}\left[f_\alpha(l)+\sum_{l'\beta}[\Phi^{(0)}_{\alpha\beta}(ll')+f_{\alpha\beta}(l,l')]v_\beta(l')+\cdots\right]u_\alpha(l)\\&+\tfrac{1}{2}\sum_{l\alpha}\sum_{l'\beta}[\Phi^{(0)}_{\alpha\beta}(ll')+f_{\alpha\beta}(ll')]u_\alpha(l)u_\beta(l')+\cdots\ .\end{aligned} \tag{B14}$$

The static displacement (lattice distortion) around the impurity atom can be determined from the condition that the linear term in the dynamic displacement $u_\alpha(l)$ should vanish:

$$\sum_{l'\beta}[\Phi^{(0)}_{\alpha\beta}(l,l')+f_{\alpha\beta}(l,l')]v_\beta(l')=-f_\alpha(l)\ . \tag{B15}$$

In the harmonic approximation, the perturbed atomic force constants are given by

$$\Phi_{\alpha\beta}(l,l')=\Phi^{(0)}_{\alpha\beta}(l,l')+f_{\alpha\beta}(l,l')\ . \tag{B16}$$

Then, the second moment μ_2 for the perturbed lattice can be obtained as follows:

$$\begin{aligned}\mu_2&=\frac{1}{3N}\sum_{l\alpha}\left[\frac{\Phi^{(0)}_{\alpha\alpha}(l,l')}{M_l}+\frac{f_{\alpha\alpha}(l,l')}{M_l}\right]\\&=\frac{1}{3NM'}\sum_{\alpha}[\Phi^{(0)}_{\alpha\alpha}(0,0)+f_{\alpha\alpha}(0,0)]\\&\quad+\frac{1}{3NM}\sum_{\alpha}\sum_{l\neq 0}[\Phi^{(0)}_{\alpha\alpha}(l,l)+f_{\alpha\alpha}(l,l)]\ .\end{aligned} \tag{B17}$$

After a bit of algebra, one can obtain the following relations for the fcc lattice with nearest-neighbor interaction,

$$\sum_{\alpha} \Phi^{(0)}_{\alpha\alpha}(0,0)=12\phi''(r_0)\ , \tag{B18}$$

$$\sum_{\alpha} f^{(0)}_{\alpha\alpha}(0,0)=12\left[\chi''(r_0)+\frac{2}{r_0}\chi'(r_0)-\phi''(r_0)\right]\ . \tag{B19}$$

Thus, we have finally

$$\delta\mu_2=\frac{4}{N}\left[\left[\frac{1}{M}+\frac{1}{M'}\right]\left[\chi''(r_0)+\frac{2}{r_0}\chi'(r_0)\right]-\frac{2}{M}\phi''(r_0)\right]\ , \tag{B20}$$

where r_0 represents the equilibrium interatomic distance.

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