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SUBMITTED TO THE GRADUATE FACULTY

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degree of

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THEODORE WESLEY RYBKA

Norman, Oklahoma

1973

THERMOELECTRIC POWER OF VACANCIES IN ALUMINUM

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I. INTRODUCTION

A. Thermopower

A voltage is produced in a circuit consisting of two metals when the junctions are at different temperatures. Usually the "cold junction" is held at some constant temperature and the temperature of the "hot junction" is varied. The circuit, of course, is called a thermocouple and the voltage is the thermoelectric voltage. The temperature derivative of this voltage is defined as the difference in thermoelectric power (or thermopower) between the two sides of the thermocouple. The two sides of a thermocouple do not have to be different metals, but can be two different states of the same metal. The measurements described here are made on a thermocouple made of one well-annealed aluminum wire and one quenched aluminum wire. The quenched wire differs from the well-annealed wire in that it contains a much larger number of vacant lattice sites referred to as vacancies. Measurement of the thermoelectric voltage and determination of the difference in thermopower for this "thermocouple" provides information on the electron scattering and on the phonon scattering from the vacancy.

B. Quenching

The number of thermally activated defects in a solid increases with temperature. In aluminum these defects are

vacancies. "Quenching" refers to the process of freezing these vacancies in the solid by lowering the temperature at such a rapid rate that the vacancies do not have time to anneal out. This is usually done by dropping the current-heated wire into a liquid quench medium. In this experiment the main quench medium was ice water although methanol was used in five cases. The quenched wire together with a well-annealed wire form the specimen "thermocouple" on which measurements are made. To avoid annealing the quenched defects, measurements must be made at low temperatures.

C. Purpose Of This Experiment

The absolute thermopower S of a metal consists of a contribution S_e , arising from the non-equilibrium distribution of the conduction electrons, and a contribution S_g , caused by the interaction between the conduction electrons and the phonons which are not in equilibrium.

$$S = S_e + S_g, \quad (1)$$

where S_e and S_g are usually called the electron-diffusion thermopower and the phonon drag thermopower, respectively.

The introduction of defects into a metal causes a change of both quantities, S_e and S_g . Call the changes ΔS_e and ΔS_g , respectively. The change in S_e depends only on the electron scattering properties and on the electronic

band structure of the system. The absolute magnitude of S_g is always reduced because the additional phonon scattering by the defects reduces the phonon current set up by the temperature gradient. An exception to this was found in 1968 by Huebener¹ when he measured the thermopower of dilute alloys of aluminum. Huebener's data for the thermopower of the alloy Al + 0.03 at.% Zn versus pure aluminum is shown as a function of temperature in Fig. 1. The convention is such that positive values of ΔS indicate a reduction in the thermopower of aluminum due to the impurities and negative values indicate an enhancement. ΔS is the total change in thermopower due to impurities and can be written as

$$\Delta S = \Delta S_e + \Delta S_g. \quad (2)$$

Huebener calculated ΔS_e using the theories available in 1968 and found it to be positive at all temperatures. This led him to conclude that at low temperatures ΔS_g was negative implying that alloying aluminum increased the phonon drag component of thermopower. He then developed a hypothesis that this was possible due to anisotropy of the electron scattering, that is if the relaxation time for the electron scattering by the impurities and the relaxation time for the electron scattering by phonons vary differently over the Fermi surface. This hypothesis can not be developed into a quantitative theory

Figure 1. Thermopower Of The Alloy

Al + 0.03 at. % Zn

(Taken from Huebener¹)

as yet and in fact its qualitative use is marginal at best.

From 1968 to 1970 Nielsen and Taylor^{2,3,4} developed a new theory of electron-diffusion thermopower which was applied to aluminum alloys by Dudenhoeffer and Bourassa⁵. The new theory provided a relatively simple explanation for Huebener's experimental data on aluminum alloys, namely that the low temperature negative peak was due to ΔS_e as calculated now using the Nielsen-Taylor theory and that the high temperature positive peak was due to ΔS_g .

The importance of determining the validity of the Nielsen-Taylor theory is readily apparent when one realizes that almost all published thermopower work involves a separation of the electron-diffusion component from phonon drag component. If the Nielsen-Taylor theory is valid, that separation has been made incorrectly in all work to date.

The measurement in this work of the thermopower of lattice vacancies in aluminum is the first experimental attempt to solve that controversy.

In addition to this controversy, vacancies in aluminum have been the center of another controversy for some time. There is evidence that divacancies play an important role in aluminum at high temperatures. Bourassa, Lazarus and Blackburn⁶ find an approximate binding energy for divacancies in aluminum of 0.5 eV.

Self-diffusion measurements performed by Seegar and Mehrer⁷ by means of radioactive isotopes suggest that divacancies and possibly also larger vacancy clusters contribute considerably to the high temperature equilibrium properties. Seegar states that the fraction of vacant lattice sites $2c_{2v}/c_{1v}$ associated in divacancies at the melting point was about 43%. Seegar reports that the binding energy is approximately 0.25 eV.

Butcher, Hutto and Ruoff⁸ have measured the activation volume for self-diffusion in Al and find $\Delta V_{\text{self-diffusion}} = 2.2 \times 10^{-23} \text{ cm}^3$. This is the only example of a vacancy activation volume which is greater than an atomic volume. Ruoff offers two possible explanations for this unusually high volume: first, that the second nearest neighbor lies in a region of repulsive force so that extraction of an atom would result in an over-all expansion of the lattice; or secondly, that the dominant equilibrium defect in aluminum is the divacancy.

On the other hand Doyama and Koehler⁹ have reported evidence of two vacancy defects in quenched aluminum; and, by assuming that they are the monovacancy and the divacancy, they estimate that the binding energy of a divacancy is 0.17 ± 0.05 eV. The experiments of Simmons and Balluffi^{10,11} measure only the total net defect concentration, c , and so can not directly distinguish between types of vacancies.

Another problem related to the one just discussed centers around the intrinsic thermopower of a vacancy in Al. Huebener¹² has measured the intrinsic thermopower of a monovacancy, $(\Delta S/c)$, in Au and found it to be $(\frac{\Delta S}{c})_{200^\circ K} = -1.67 \pm 0.03 \text{ } \mu V/^\circ K \text{ at. \%}$. A similar measurement has not been made in Al. One experiment⁶ has indicated that the intrinsic thermopower of a vacancy in Al may be as high as $+130 \text{ } \mu V/^\circ K \text{ at. \%}$. Such a high value of $(\Delta S/c)$ would strongly indicate the presence of divacancies. This work does not answer the divacancy controversy, but it does give evidence that thermopower measurements are very sensitive to the type of defect present.

In this experiment the difference in thermoelectric voltage between a well-annealed aluminum wire and an aluminum wire containing vacancies was measured as a function of temperature from $4.2^\circ K$ to $150^\circ K$, and the difference in thermopower, ΔS , between the two wires was determined. These results will be presented in Chapter IV. The analysis of the data centers around two theories of separation of the data into the electron-diffusion component, ΔS_e , and the phonon drag component, ΔS_g . These two separation theories are discussed in Chapter II.

II. THEORY

A. Thermopower Relationships

The electron-diffusion thermopower of a metal is given by

$$S_e = -S_o \left[\frac{\partial \ln \rho(\epsilon)}{\partial \ln \epsilon} \right]_{\zeta}, \quad (3)$$

with

$$S_o = \frac{\pi^2 k_B^2 T}{3e\zeta}, \quad (4)$$

where e is the (negative) electronic charge, k_B is Boltzmann's constant, T is the absolute temperature, ϵ is the hypothetical height of the Fermi level, ζ is the Fermi energy, and $\rho(\epsilon)$ is the electrical resistivity of the metal.

The quantity in the square brackets is usually taken to be independent of temperature so that as a first approximation the electron-diffusion thermopower is often expressed as directly proportional to the temperature. This approximation will be used at one point in Section B.

Consider a metal containing point defects. If the concentration of these defects is small (less than 1% of the number of host-metal atoms usually), the system is referred to as dilute. The system considered here is dilute and the defects are vacancies, missing atoms in the lattice structure of the metal.

In dilute metallic systems the defects can be treated to a good approximation as independent and the resistivity of the system, ρ , is given by the resistivity of the host lattice, ρ_o , plus the resistivity of the defects, $\Delta\rho$. This is written as

$$\rho = \rho_o + \Delta\rho \quad (5)$$

and is known as Matthieson's rule¹³. The electron-diffusion thermopower, S_e , of a dilute metal is then given by

$$S_e = - S_o \left[\frac{\partial \ln \{ \rho_o(\epsilon) + \Delta\rho(\epsilon) \}}{\partial \ln \epsilon} \right]_{\zeta} \quad (6)$$

It follows that,

$$S_e = \frac{\rho_o}{\rho} S_e^o + \frac{\Delta\rho}{\rho} S_e^i, \quad (7)$$

where

$$S_e^i = - S_o \left[\frac{\partial \ln \Delta\rho}{\partial \ln \epsilon} \right]_{\zeta}, \quad (8)$$

and

$$S_e^o = - S_o \left[\frac{\partial \ln \rho_o}{\partial \ln \epsilon} \right]_{\zeta} \quad (9)$$

S_e^o is the electron-diffusion thermopower of the pure metal, and S_e^i is identified as the intrinsic electron-diffusion thermopower of the defect.

The change ΔS in the thermopower of a metal due to defects was given in Eq. (2) as,

$$\Delta S = \Delta S_e + \Delta S_g, \quad (2)$$

where ΔS_e and ΔS_g are the change in the electron-diffusion and the phonon drag thermopower, respectively.

ΔS_e is defined as

$$\Delta S_e \equiv S_e - S_e^0. \quad (10)$$

Then from Eqs. (6), (9) and (10)

$$\Delta S_e = \frac{S_e^0}{(\rho_0/\Delta\rho)+1} \left[\frac{(1/\Delta\rho) (\partial\Delta\rho/\partial\varepsilon)}{(1/\rho_0) (\partial\rho_0/\partial\varepsilon)} - 1 \right] \zeta. \quad (11)$$

It is at this point that the two methods of electron-diffusion separation arise. In the first method to be discussed the quantity in the square brackets is assumed to be independent of temperature¹². In the second method, developed by Nielsen and Taylor, a significant temperature dependence is predicted. In either case the square bracket can be written as,

$$H = \left[\frac{(1/\Delta\rho) (\partial\Delta\rho/\partial\varepsilon)}{(1/\rho_0) (\partial\rho_0/\partial\varepsilon)} - 1 \right] \zeta. \quad (12)$$

Then,

$$\Delta S_e = \frac{S_e^0}{(\rho_0/\Delta\rho)+1} H. \quad (13)$$

B. Determination Of The Change In Electron-Diffusion

Thermopower: Method I

At high temperatures S_g^0 and ΔS_g are assumed to be negligible because phonon-phonon collisions dominate and reduce the phonon drag thermopower. Therefore, in a metal without impurities where S is the measured thermopower of the metal,

$$S_e^0 = S_e = S, \quad (14)$$

and

$$\Delta S_e = \Delta S. \quad (15)$$

S_e^0 versus T can be determined as follows. As mentioned in Section A, S_e^0 can be approximated as,

$$S_e^0/T \approx \text{constant}. \quad (16)$$

At high temperatures Eq. (14) holds. The constant (S_e^0/T) can then be evaluated using the experimental plot of S versus T .

Now using Eqs. (13) and (15), together with the experimental value of ΔS , a value for H can be obtained at high temperatures.

Using this value of H , the values of ΔS_e versus temperature can be deduced from Eq. (13).

ΔS_g is obtained from Eq. (2). This separation was carried out for the data obtained in this experiment and will be discussed in Chapters IV and V.

**Figure 2. Absolute Thermopower Curve For
Aluminum**

**(Taken from Gripshover, VanZytveld
and Bass³⁴)**

C. Determination Of The Change In Electron-Diffusion

Thermopower: Method II

The Nielsen-Taylor theory gives an alternate method for determination of the change in the electron-diffusion thermopower.

Nielsen and Taylor^{2,3,4} have applied second order corrections to the T-matrix for electron scattering involving intermediate virtual phonon states. Their results gave an additional contribution to the electron-diffusion thermopower of a metal which has the same magnitude and general temperature-dependence as that attributed to phonon drag. Nielsen and Taylor have also demonstrated the importance of this concept to the electron-diffusion thermopower of dilute alloys.

Experiments done in dilute aluminum alloys¹ show that the thermopower on alloying is enhanced rather than reduced in the region of the negative minimum. One expects a reduction in the magnitude of the phonon drag thermopower whenever any scattering center is introduced into a metal. This is because the magnitude of the phonon drag contribution to the thermopower is dependent upon the relative probability that a phonon will scatter with an electron as opposed to all other scattering mechanisms¹⁴. Adding impurities gives rise to the possibility of phonon impurity scattering and thus reduces the phonon drag thermopower.

Hence the aluminum alloy results indicate that the negative minimum in ΔS may not be due to phonon drag as was assumed by Huebener but may indeed be by the additional contribution to the electron-diffusion component as predicted by Nielsen and Taylor.

The Nielsen-Taylor theory has been used by Dudenhoeffer and Bourassa to calculate the electron-diffusion component in dilute aluminum alloys⁵. Comparison with experiment showed qualitative agreement. It was found that for dilute aluminum alloys the Nielsen-Taylor theory predicts the correct sign and the approximate location of the negative minimum in ΔS .

Nielsen and Taylor use a free electron model. The electrical resistivity is written as

$$\rho(\epsilon) \propto 1 / \left(v^2(\epsilon) \tau(\epsilon) N(\epsilon) \right) \quad (17)$$

where $\tau(\epsilon)$ is the electron relaxation time, $v(\epsilon)$ is the electron velocity, and $N(\epsilon)$ is the density of states. In a system of free electrons, both $v(\epsilon)$ and $N(\epsilon)$ are proportional to $\epsilon^{1/2}$. Thus

$$\left[\frac{\partial \ln \rho(\epsilon)}{\partial \ln \epsilon} \right]_{\zeta} = \left[\frac{\partial \ln 1/\tau}{\partial \ln \epsilon} \right]_{\zeta} - \frac{3}{2} \quad (18)$$

τ can be expressed in terms of τ_1 , the relaxation time for electron phonon scattering and τ_2 , the relaxation time for electron impurity scattering as

$$1/\tau = 1/\tau_1 + 1/\tau_2 \quad . \quad (19)$$

This is another form of Matthieson's rule and from Eq. (17) and Eq. (18) one can write

$$\left[\frac{\partial \ln \rho_o}{\partial \ln \epsilon} \right]_{\zeta} = D_1 - \frac{3}{2} \quad , \quad (20)$$

and

$$\left[\frac{\partial \ln \Delta \rho}{\partial \ln \epsilon} \right]_{\zeta} = D_2 - \frac{3}{2} \quad , \quad (21)$$

where

$$D_i \equiv \left[\frac{\partial \ln 1/\tau_i}{\partial \ln \epsilon} \right]_{\zeta} \quad i = 1, 2 \quad . \quad (22)$$

Eq. (9) and Eq. (11) can now be rewritten as

$$S_e^o = S_o \left(\frac{3}{2} - D_1 \right) \quad , \quad (23)$$

and

$$\Delta S_e = \frac{S_e^o}{\rho_o/\Delta \rho + 1} \left(\frac{D_2 - 3/2}{D_1 - 3/2} - 1 \right) \quad . \quad (24)$$

Rearranging terms in Eq. (24) and making use of Eq. (23) gives

$$\Delta S_e = \frac{S_o}{(\rho_o/\Delta \rho) + 1} (D_1 - D_2) \quad . \quad (25)$$

The contribution of Nielsen and Taylor enters at this point through the calculation of D_1 and D_2 . Their calculation of D_1 is unsatisfactory for quantitative calculations since Umklapp scattering was neglected. Dudenhoeffer and Bourassa used the pure metal experimental data for S_e^0 to compute D_1 via Eq. (23) and that method will also be used in this work.

The expression for D_2 as calculated by Nielsen and Taylor is

$$D_2 = \frac{1}{2} + 2 \left. \frac{\partial \ln \mathcal{U}}{\partial \ln \epsilon} \right|_{\zeta} + \frac{9 \mathcal{U}}{4 k_B T} \frac{m}{M} \frac{N'}{N} \Psi\left(\frac{T}{\theta}\right) + \frac{2}{3} \frac{\mathcal{V} \zeta}{4 k_B T (k_B \theta)} \frac{m}{M} \left(\frac{2N}{N'}\right)^{1/3} L_2\left(\frac{2T}{\theta}\right), \quad (26)$$

where θ is the Debye temperature, N is the number of ions in the sample, N' is the number of electrons in the sample, m/M is the ratio of electronic to ionic masses, $\mathcal{V}$ is the pseudopotential of the host, $\mathcal{U}$ is the renormalized pseudopotential appropriate to the dilute alloy, and $\Psi(\frac{T}{\theta})$ and $L_2(\frac{2T}{\theta})$ are complicated functions of temperature².

The pseudopotential $\mathcal{U}$ appropriate to the dilute alloy was obtained from the expression

$$\mathcal{U}^2 = 4 \int_0^1 U^2(z) z^3 dz, \quad (27)$$

where

$$z = q/2k_F \quad , \quad (28)$$

k_F being the Fermi radius and,

$$U(z) = \frac{\Omega_2}{\Omega_1} V_2(z) - V_1(z) \quad . \quad (29)$$

The quantities $V_1(z)$ and $V_2(z)$ are the pseudopotentials of the host and solute, respectively, calculated by Animalu and Heine¹⁵, as quoted by Harrison¹⁶; the quantities Ω_1 , and Ω_2 are the atomic volumes of the host and the solute, respectively. For vacancies in aluminum $V_2(z)$ was set equal to zero. Nielsen and Taylor² developed the expression for $\mathcal{U}^2$ given above. However, they took $U(z)$ to be constant and evaluated it at $z = 0$. This can lead to large errors for some alloys. The sign of $\mathcal{U}$ was taken as the sign of the values of $U(z)$ which make the major contribution to $\mathcal{U}$.

$$\mathcal{U}^2 = \frac{\int_0^{z_D} |V_1(z)|^2 z^4 \operatorname{csch}\left(\frac{\Theta z}{T z_D}\right) dz}{\int_0^{z_D} z^4 \operatorname{csch}\left(\frac{\Theta z}{T z_D}\right) dz} \quad , \quad (30)$$

where $z_D = \frac{q_D}{2k_F}$, q_D being the Debye cutoff. This expression was developed by Nielsen and Taylor², although they again took $V_1(z)$ as a constant and removed it from the integral.

The change in thermopower, ΔS_e , calculated using the Nielsen-Taylor theory will be denoted as ΔS_e^{NT} . The determination of ΔS_e^{NT} was carried out and is presented in Chapter IV. The values of ΔS_g were then determined by subtracting ΔS_e^{NT} from the total measured ΔS . These results are discussed in Chapter V.

D. Estimation Of The Rayleigh Scattering Parameter For Phonon Scattering From Vacancies

In the 19th century, Lord Rayleigh investigated the scattering of light waves by a particle much smaller than their wavelength¹⁷. He found that the scattered wave amplitude should be proportional directly to the volume of the particle and inversely to the square of the wavelength. The scattered intensity is thus proportional to the inverse fourth power of the wavelength.

Rayleigh scattering is also the process responsible for the X-ray scattering by atoms used in X-ray crystallography. If the wavelength is appreciably greater than the dimensions of the atom, the atom acts in the same way as Rayleigh's small particle. Each of the extra-nuclear electrons oscillates in the electromagnetic field of the incident wave and re-radiates it.

In a solid a defect of atomic dimensions¹⁸, such as a vacant lattice site, will upset the regularity of the

crystal lattice. At low temperatures this irregularity will be very much smaller than the phonon wavelength and the scattering which it produces is analogous to the Rayleigh scattering of optics and atomic physics discussed above. Rayleigh's treatment thus may be used and this gives a scattering probability which is proportional to the fourth power of the phonon wave vector q . A derivation of this fourth power relationship between the cross section and wave vector q was given by Lord Rayleigh¹⁹. It can be shown that this is equivalent to an inverse fourth power relationship between the phonon relaxation time, τ_1 , and the frequency ω ²⁰. The constant of proportionality is called the Rayleigh scattering parameter, a . The actual magnitude of the scattering will be determined by the difference in density and in elastic constant which are caused by the scattering center in the lattice.

The Rayleigh scattering parameter, a , appears in theoretical expressions for phonon-relaxation time, τ_1 , which in turn appears in expressions for electrical resistance, thermopower, thermoconductivity and other transport properties. Thus it is important that the experimental value of a be known.

In this Section an expression for the change in phonon drag thermopower, ΔS_g , in terms of the Rayleigh

scattering parameter, a , will be developed. This expression will be used in Chapter IV to show that the broad maximum in the thermopower curves found above 80 °K is due to phonon drag. The analysis will be presented in detail in Chapter IV, but it is perhaps appropriate at this point to briefly describe the procedure that will be used.

Using the experimental value of ΔS at 100 °K a value of the scattering parameter, a , will be determined for both Method I and Method II. These values will be compared to theoretical values that will be developed using the theories of Klemens²¹ and Carruthers²² which are described below. The scattering parameters obtained by Method I and Method II will be used to calculate the temperature dependence of ΔS_g and this prediction will be compared to the experimental data.

The phonon drag component of the thermopower of a pure metal, S_g^0 , can be expressed as a superposition of contributions from each phonon present in the metal and can be written as

$$S_g^0 = \sum_j \int s_g(\underline{q}, j) d^3q, \quad (31)$$

where $\underline{q}$ is the phonon wave vector, j the polarization of the phonon, and $s_g(\underline{q}, j)$ is the phonon drag thermopower associated with the phonons $\underline{q}, j$.

The change of the phonon drag thermopower due to phonon scattering by lattice defects is given by Huebener¹² as,

$$\Delta S_g \equiv S_g - S_g^0 = - \sum_j \int \frac{s_g(q,j) d^3q}{1 + \tau_i(q,j)/\tau_0(q,j)} , \quad (32)$$

where $\tau_i(q,j)$ is the relaxation time for phonon scattering by the defects and $\tau_0(q,j)$ is the relaxation time for phonon scattering in the pure material.

It was necessary to obtain expressions for τ_0 and s_g . τ_0 is included in the theoretical expression for the lattice thermal conductivity K_L . From the Debye theory and elementary kinetic theory²³ K_L is given by,

$$K_L = \frac{k_B}{2\pi^2 v_s} \left(\frac{k_B T}{h} \right)^3 \int_0^{\theta/T} \frac{\tau_0 z^4 e^z}{(e^z - 1)^2} dz , \quad (33)$$

where v_s is the sound velocity in the crystal,

$$z = \frac{h\omega(q,j)}{k_B T} , \quad (34)$$

and ω is the phonon frequency. The expression used for τ_0 is of the form developed by Pohl and Walker²⁴:

$$\tau_0^{-1} = b\omega^2 T e^{-\beta/T} . \quad (35)$$

The two constants, b and β have been determined by putting in the experimental value for K_L and obtaining the best fit.

In order to determine s_g , another expression for S_g^0 was necessary. Huebener¹² developed an expression given by

$$S_g^0 = A e^{\beta/T} \int_0^{\theta/T} \frac{z^2 e^z}{(e^z - 1)^2} dz \quad (36)$$

The constant A was found by fitting the expression on the right in Eq. (36) to the appropriate experimental value of S_g^0 .

Using Eq. (31) and Eq. (36), the expression for s_g was identified as,

$$s_g(q) = \frac{A}{4\pi} e^{\beta/T} \left(\frac{\hbar v_s}{k_B T} \right)^3 \frac{e^z}{(e^z - 1)^2} \quad (37)$$

Then assuming a pure Rayleigh scattering mechanism, it follows from earlier considerations that,

$$\tau_1^{-1} = a \omega^4, \quad (38)$$

where a is the scattering parameter and ω is the phonon frequency.

Using the expressions for s_g , τ_0 , and τ_1 in Eq. (32), one obtains

$$\Delta S_g = -Ae^{\beta/T} \int_0^{\theta/T} \frac{z^2 e^z}{(e^z - 1)^2} \left[1 + \frac{b\hbar^2 e^{-\beta/T}}{ak_B^2 z^2 T} \right]^{-1} dz \quad (39)$$

By fitting the right hand side of Eq. (39) to the experimentally determined value for ΔS_g , a value for the scattering parameter, a , has been obtained.

The value of the scattering parameter a obtained in this way is to be compared with the values of a predicted by Klemen's theory and Carruthers' theory.

Using second order perturbation theory, Klemens obtained an expression for a :

$$a = \frac{3\Omega c^*}{\pi v_s} L^2, \quad (40)$$

where,

$$L^2 = \frac{1}{12} \left[\frac{\Delta M}{M} \right]^2 + \left[\frac{1}{\sqrt{6}} \frac{\Delta F}{F} - \left(\frac{2}{3} \right)^{\frac{1}{2}} Q\gamma \frac{\Delta R}{R} \right]^2, \quad (41)$$

and Ω is the atomic volume of the crystal, c^* is the mole fraction of the point defects, γ is the Grüneisen constant, M is the atomic mass of the crystal, F is the force constant

of a linkage, R is the nearest neighbor distance. ΔM , ΔF , ΔR are changes in these quantities at the location of the point defects and Q is the contribution to the scattering matrix from strain outside the six nearest neighbors.

For strain field scattering Carruthers obtained the same Eq. (40) as did Klemens, but his expression for L differed. Carruthers' expression for L^2 was,

$$L^2 = 80\gamma^2 \left(\frac{\Delta R}{R} \right) \quad . \quad (42)$$

E. Point Defects In Metals: Quenching Techniques

Point defects can be introduced into the host material by alloying, by coldworking, by irradiation, by ion implantation, by pressure and by quenching. There are many types of point defects that occur in metals. They are impurity atoms, vacancies, interstitials, vacancy clusters, loops and voids. In this work the primary interest is vacancies and their effect on the thermopower of aluminum. The quenching technique can introduce vacancies into a metal almost exclusively of other defects.

When a metal is sufficiently heated, vacancies are formed from the supplied thermal energy. The thermal

equilibrium concentration, c , of vacancies in the metal at temperature T is given by

$$c = c_0 e^{-E_f/k_B T}, \quad (43)$$

where c_0 is the number of lattice sites in the metal, and E_f is the formation energy of a vacancy. The maximum value of c/c_0 occurs at the melting point and is given by Simmons and Balluffi^{10,25} in their equilibrium measurement as 7×10^{-4} for gold and 9.4×10^{-4} for aluminum.

Actually more than one type of vacancy exists in thermal equilibrium at elevated temperatures so that a more general expression is required.

$$c_v = c_{1v} + 2c_{2v} + \dots + nc_{nv}, \quad (44)$$

where the c_{nv} are the concentrations associated with each type of vacancy. However, only c_{1v} , the monovacancy concentration and c_{2v} , the divacancy concentration, will be considered. It is expected that $c_{2v} \ll c_{1v}$ for most situations.

In the expression for c_v , there is to date no experimental way in which to measure the relative contributions of the c_{iv} , $i = 1 \dots n$, to the total vacancy concentration c_v . This is most distressing as it is impossible at

present to categorically say what the effect of each vacancy component is on a particular transport property.

When the metal specimen, usually in wire form or as a thin foil, is quenched the vacancies that are in thermal equilibrium at elevated temperatures are "frozen-in", that is they become immobilized, due to the rapid dropping of temperature of the metal host. This rapid drop is achieved by immersing the specimen into a liquid or gas which is at a much lower temperature. If the quenching speed is rapid the distribution of point defects after the quench approximates the distribution before the quench.

It is believed that the equilibrium distribution should be primarily monovacancies or monovacancies and divacancies at the higher temperatures. During the quench monovacancies and divacancies can anneal out to the line dislocations grain boundaries or other sinks which may be present. Divacancies can break up into monovacancies. Divacancies can interact with other divacancies or monovacancies and form clusters. Thus nucleation or growth of clusters can occur. This then means that the original point defect distribution present in thermal equilibrium before the quench has been changed and the distribution which exists at the low temperatures is somewhat different.

Thus there may be some losses during quenching as well as a redistribution of monovacancies and divacancies.

Ideally, one tries to retain the equilibrium distribution. How well this aim is achieved will have to await direct evidence from possible future field-ion measurements. However, it is presently known through electron microscope measurements by Meshii²⁶ that large loops and clusters are not introduced in the specimen due to the quenching technique as outlined.

The vacancies introduced into the metal, in this case by quenching, have a significant effect on its transport properties, in particular on the resistance and the thermopower. The increase in electrical resistivity commonly called the quenched-in resistivity $\Delta\rho$ can be expressed as,

$$\Delta\rho = Ae^{-E_f/k_B T} . \quad (45)$$

Equation (13) can be written as,

$$\Delta S_e = S_e^0 \frac{\Delta\rho}{\rho} H . \quad (46)$$

Since it is known from experiment that $\Delta\rho$ is independent of temperature the assumptions that H is independent of temperature and that both S_e^0 and ρ are linear in temperature result in the following relation:

$$\Delta S_e \approx \text{constant} \times \Delta\rho . \quad (47)$$

This equation should hold at all temperatures according to Method I, but should only hold at high temperatures according to Method II since the temperature dependence of ΔS_e predicted by Nielsen and Taylor² decreases above 30 °K.

Using Eqs. (45) and (47), the electron-diffusion thermopower can be written as,

$$\Delta S_e \approx A'e^{-E_f/k_B T} \quad (48)$$

The quench rate is an important parameter in quenching experiments. This is pointed up in the results of calculations of a quench model used by Doyama²⁷. Different quenching media give different quench rates. Typical quenching media used are ice and water, brine, water and calcium chloride, methanol and dry ice, liquid nitrogen, and air. Bass²⁸ has measured quench rates in aluminum for different media and found quench times which range from 10 milliseconds to 2.0 seconds for typical quench temperatures.

The conventional way of measuring the vacancy concentration is to measure the quenched-in resistivity at liquid helium temperatures. Simmons and Balluffi^{10,11,25} have determined the concentration of a vacancy in gold and in aluminum by measuring the change in the lattice constant and the change in volume of the metal as a function of temperature.

Using their value and the measured value of the quenched-in resistivity, the vacancy concentration can be

deduced. The assumption is made that the quenching conditions are such that only one type of point defect is present, namely the monovacancy.

There has been a vast amount of work done on annealing experiments²⁷. The quenched-in resistivity is allowed to anneal out at some particular annealing temperature and the resistivity ratio, i.e. the initial resistivity to the resistivity at some later time is measured. Two basic types of annealing experiments are (1) isothermal experiments in which the annealing temperature is kept constant with time and (2) isochronal experiments in which the annealing temperature is increased in constant intervals of time.

These experiments give information on formation energy E_f , migration energy E_m , and other parameters as well. The isochronal curves are important because they give the approximate temperature above which the supersaturated vacancies cease to be immobile and can move sufficiently rapidly to anneal out. This temperature is 0 °C for gold but is -60 °C for aluminum for a quench temperature of about 500 °C²⁷. These temperatures become even lower as the quench temperature is increased. Thus for the case of aluminum the wire temperature must not exceed -100 °C in order to be certain that essentially no supersaturated vacancies begin to anneal out in the time

period involved in the experiment.

Many quenching experiments in which only the resistance was measured have been done. Many experiments which have measured the thermopower change due to dilute alloying have been done. Only a very few experiments have been done which have measured the thermopower of vacancies in pure metals, namely one experiment on gold and one on platinum. Retention of vacancies in aluminum presents a much more difficult problem.

III. EXPERIMENTAL APPARATUS AND PROCEDURES

A. Elements Of The Apparatus

The apparatus was composed of a specimen, sample holder, copper can, connecting vacuum plate, upper inner assembly, the cryostat and the measuring instruments. The sample holder, connecting vacuum plate and copper can formed the lower inner assembly. See Fig. 3.

B. Specimen Make-Up

Aluminum wire of 6 9's purity was procured from Cominco, Spokane, Washington. In order to spot-weld aluminum it was necessary to acid etch the wires for four minutes in an 8% hydrofluoric acid solution, rinse off the acid in distilled water and then rinse again in methanol. An Ewald welder, Model WHDSA, was used to perform the spot-welds. The specimen wires were 0.010 in. in diameter, the holder wires were .018 in. in diameter, and the wire forming the junctions were .005 in. in diameter. Fig. 4 shows the arrangement of the wires in the specimen.

C. Sample Holder

1. Elements of the holder: The design of the sample holder was patterned after that of Huebener's¹². The holder and its specimen consisted of a hot junction,

Figure 3. Inner Assembly Schematic

1. Electrical Terminals
2. Upper Inner Assembly
3. Connecting Vacuum Plate
4. Sample Holder
5. Vacuum Can
6. Lower Assembly
7. Lower Indium O-Ring Seal
8. Upper Indium O-Ring Seal
9. Electrical Leads

Figure 4. A. SPECIMEN

1. .005 In. Junction Wire
2. Expansion Loop
3. Specimen Wire
4. Holder Wires
5. Lower Junction (Hot, Variable)
6. Well-Annealed Lead
7. Upper Junction (Cold, Fixed)

B. SAMPLE HOLDER

8. Terminals Block
9. Heat Sink
10. Thin Wall Stainless Steel Tubing
11. Thermocouple
12. Heater

Specimen And Sample Holder Shown
Separately For Clarity

A

B

a cold junction, a heater, a heat sink and terminal blocks. One of the requirements was that there be good thermal conductivity but high electrical insulation between the aluminum wires of the specimen and various parts of the sample holder. General Electric 7031 adhesive and insulating varnish has these properties and was used in our early experiments. In later experiments using methanol either as a quench medium or in the quenching procedure, it became necessary to find some other material for the insulative, high thermal conductance coatings since varnish is attacked by methanol. Emerson and Cuming 2850 GT stycast was used to make these coatings since it met the requirements and yet was not attacked by methanol. Apiezon N grease or Dow-Corning high vacuum grease further improved the thermal conductivity and was used on all clamping surfaces. Stainless steel tubing having a 0.010 in. wall thickness was used in the frame providing structural strength and low thermal conductivity.

The heater consisted of a small copper block around which fifteen turns of 0.003 in. diameter Evanohm insulated wire was wound. The resistance of the winding was 1000 ohms and the maximum current needed to produce the required temperature gradients was 30 milliamps.

2. Pressure Junctions: It was not desirable to spot-weld after quenching since quenched-in vacancies

in aluminum rapidly disappear at room temperatures when compared to, say, vacancies in gold. Instead a pressure junction was formed by clamping in a low temperature liquid medium. Huebener used this method in his alloy work in aluminum¹.

It was necessary to anneal the specimen and potential lead wire without having the hot or cold junction clamped so that the temperature was uniform along the wire between the two junctions. Clamping would supply large heat sinks to the wire destroying the uniform temperature along the wire. Since it was necessary to determine the annealing temperature of the wire specimen, .005 in. wires spot-welded at the two junctions before quenching provided electrical contact for this measurement without creating a significant heat sink.

D. Connecting Vacuum Plate

1. Purpose: This unit was an interface device. It interfaced with the sample holder, upper inner assembly, and the vacuum can. It was used to form a seal with a copper can and so provided a vacuum-tight enclosure for the specimen. It also routed the electrical leads, by means of low temperature electrical feed-throughs, from inside a high vacuum region to an unpressurized region; this was done at cryogenic temperatures and in a liquid

helium bath. This unit also formed a vacuum seal for a pump line necessary to evacuate the copper can. Note that the copper can seal and electrical feed-through seal were spatially displaced from the pump line seal.

In addition this plate supported the sample holder and provided a heat sink for the upper junction of the specimen. The thermal conductance between the heat sink and the liquid helium bath in which one side of the brass plate was immersed was very high so that the temperature of the upper junction was held between 4.2 °K and 5.2 °K.

2. Low Temperature Electrical Feed-Throughs:

Two feed-throughs were fabricated following the design of A. C. Anderson²⁹. In the latest design modification one feed-through consisted of seven wires and the other of eight. The metals used for the wires were copper, aluminum, gold and chromel. The wire diameters ranged from .010 in. to .035 in. The .035 in. wires were used to carry 6 amperes of annealing current. Extreme care was required in fabrication. These seals were still functioning satisfactorily after being thermally cycled many times and subjected to thermal shock. Note that the part of the wire which was in contact with the stycast sealing compound was stripped of the insulative varnish to insure a better seal.

E. Upper Inner Assembly

This unit routed electrical leads from the lower assembly, i.e. from the sample holder to the leads coming from the measuring instruments. This unit also provided a pump line down to the lower assembly, formed a demountable cryogenic vacuum seal with it, and mechanically supported the lower assembly. The upper inner assembly was also used to position the specimen in the cryostat at the proper depth. Vacuum seals were made with indium O-rings.

F. Cryostat

Refer to Fig. 5. The cryostat was constructed from two large dewars manufactured by Scientific Glass Blowing Co., Inc. of Houston, Texas; one dewar was positioned inside the other concentrically about the vertical axis. The inner dewar was sealed at the top by means of a copper collar. Thus the inner chamber could be evacuated and back-filled with helium or nitrogen gas. The inner dewar had a valved jacket so that the jacket could be evacuated or back-filled with nitrogen gas. The system was designed to achieve temperatures as low as 4.2 °K. The cryostat used either a liquid helium bath or a liquid nitrogen bath in the inner chamber.

Figure 5. Cryostat Section

1. Copper Collar
2. Fixed Surface
3. Dewar Mounting Flange
4. Jacket Valve
5. Inner Dewar Chamber
6. Inner Dewar Jacket
7. Outer Dewar Chamber
8. 3.35 In. I.D.
9. 5.7 In. I.D.
10. 118 Inches
11. Inner Chamber Pump Coupling
12. Vacuum Can Pump Coupling

Figure 6. Measuring Instruments

A. Thermoelectric Voltage Measurement

B. Temperature Voltage Measurement

A. B.

G. Measurement Instruments

A Guildline 9176-G nanovolt potentiometer was used to measure the very small thermovoltages of this work. It has theoretical sensitivity of 10^{-9} volts and in this application has given stable readings of 5×10^{-9} volts. During measurement the galvanometer was reversed. This eliminated from the reading the effects of thermal emfs in the galvanometer and galvanometer leads. A Guildline 9461-A galvanometer and a Guildline 9460-A photoelectric nanovolt amplifier were associated with this instrument.

A Leeds and Northrup Type K-4 potentiometer together with a Leeds and Northrup D. C. null detector were used to measure the hot junction thermocouple voltages. The sensitivity of this instrument is 10^{-7} volts. The K-4 instrument was also used to monitor the heat sink temperature. The circuitries used for measurement are shown in Fig. 6.

In the single gradient experiment described in Section I, a continuous record of thermovoltage with time was required. In order to provide the necessary linear signal for recording, the output of the Guildline nanovoltmeter was connected to a Keithly 147 nanovolt null detector which amplified the signal. That amplified voltage was then recorded with a Hewlett Packard 7034-A X-Y recorder.

H. Annealing And Quenching Procedure

1. D. C. Annealing Technique: The Specimen and the two potential lead wires were annealed by passing a d. c. current through them. It is estimated that the temperature along the length of the wire was uniform to $\pm 5\%$. The potential lead wires were heated at more than 525°C for $1\frac{1}{2}$ hours. The temperature was reduced continuously over a period of 20 minutes to approximately 150°C . The potential lead wires were then air quenched to room temperature to prevent void formation. The specimen wire was similarly heat treated and was then annealed at the particular temperature of interest for $1\frac{1}{2}$ hours before quenching. This heat treatment follows that used by Bass²⁸.

2. Determination Of Room Temperature Resistance:

The resistance of the specimen wire was determined by measuring the voltage across the specimen when a known current passes through it. The current was determined by measuring the voltage across a Leeds and Northrup 1 ohm standard resistance. The value of current used was nominally 27 milliamps. The resistance of the well-annealed wire was also measured. This information was used to compute the quenched-in resistivity and the annealing temperature prior to quench, T_Q . The room temperature is also recorded. The same circuitry and technique is used

Figure 7. A. Room Temperature Resistance
Measurement

B. Annealing Temperature Resistance
Measurement

49

A

B

to measure the resistance of the specimen wire and well-annealed wire at 4.2 °K.

3. Evaluation Of The Annealing Temperature:

The resistivity of the specimen at the annealing temperature was determined and compared to the resistivity versus temperature data of Simmons and Balluffi¹¹. The maximum value of current used in annealing was about 6 amperes. The annealing current value was obtained by measuring the voltage across a Leeds and Northrup 0.01Ω standard resistance which was immersed in a stirred oil bath.

4. Quenching Principles And Technique: In

quenching it is important that all parts of the wire enter simultaneously and that the wire remain in motion while the wire is cooling to ensure a rapid quench³⁰. Strain introduced in the wire during the quench can be minimized by making the distance of the specimen wire from the quench surface as small as possible, about 1 to 2 centimeters. It was found that expansion loops (see Fig. 4) reduce specimen distortion during annealing.

The wire was quenched by throwing a switch which then activated a solenoid which released the specimen so that it fell under the action of gravity into the quench medium. Immediately after the specimen was immersed, the current flowing through the wire was interrupted by

manually opening a switch. From quench rate measurements in a distilled ice and water medium, it was evident that the quenching action was achieved by the wire entering the quench medium even though the annealing current was still on. This is also discussed by Bauerle and Koehler³⁰. The measured value of the quench rate in a distilled ice and water mixture was 2.5×10^4 °C/sec.

I. Quenching Media And Procedures Used

1. Water-To-Methanol Quench: After the quench it is vital that the specimen be lowered in temperature as rapidly as possible. If the quench rate is large enough, then the equilibrium temperature vacancy distribution is retained. The fastest quench procedure in this experiment was obtained in the following manner.

First, the specimen was quenched into a medium of distilled ice and distilled water. After this first stage quench (time duration < 1 second) the specimen was transferred from the ice and water bath into a second bath of dry ice and methanol at a temperature of -80 °C. The transfer was made as rapidly as possible; the transfer time from the first stage quench until specimen immersion in the cold methanol was < 15 seconds.

In his work on quenching in aluminum, Bass²⁸ found no systematic differences between data taken on wires

Figure 8. Quench Tank With Quenching Assembly

1. Pivot Axis
2. Connecting Vacuum Plate
3. Five Gallon Aquarium Tank
4. Electrical Feed-Through
5. Quenching Medium
6. Cover
7. Specimen And Holder (Unclamped Position)
8. Heated Specimen Wire
9. Solenoid
10. Release Bar
11. Quench Lever
12. Quenching Leads
13. Terminals

quenched to 0 °C, -40 °C or -50 °C, provided that the wires were quickly (10 to 15 seconds) immersed in liquid nitrogen.

After the second stage quench, i.e. specimen immersion into the methanol, the hot and cold junctions and the heater unit were clamped in the -80 °C liquid.

The copper can with the lower O-ring in place was completely lowered into the methanol bath and allowed to cool. The specimen and sample holder which was connected to the quench lever (see Fig. 8) was inserted into the copper can. This operation was performed with the specimen wire at all times submerged in the cold methanol. The quenching leads and quench lever were then removed.

The lower O-ring seal was made, the liquid within the copper can was drained and nitrogen gas was introduced into the can to inhibit atmospheric condensates from forming inside the can and creating troublesome outgassing problems later on. At the same time the outside of the can was placed in contact with a liquid nitrogen bath up to approximately the flange. Cooling the specimen by gas and solid conduction from the methanol bath temperature (-80 °C) to near liquid nitrogen temperatures (77 °K) can be considered the third stage of the quench. The upper inner assembly was positioned over this nitrogen bath and was connected to a pumping system. Upon removing the

nitrogen gas the upper O-ring seal was made, and the copper can was evacuated. Electrical connections were made at the connecting vacuum plate. Then the inner assembly was complete.

The inner assembly was then inserted into the cryostat which has been cooled to liquid nitrogen temperatures and electrical connections were made to the measuring instruments.

This procedure can be described as a three stage quench. Refer to the schematic in Fig. 9.

2. Methanol Quench: Several runs were made using a methanol and dry ice mixture as the first stage quench medium. After the quench, the hot and cold junctions and the heater unit were clamped in the medium at a temperature of -80°C . The specimen was then inserted into the copper can which was already immersed in the quench medium. The procedure then followed that of the water-to-methanol quench.

The methanol quench procedure had the advantage that the specimen was quenched to a much lower temperature, namely -80°C , but it had a major disadvantage in that the quench rate was not as fast as for the water-to-methanol quench. The schematic shown in Fig. 9 gives a temperature history of the quench.

3. Single Gradient Measurement: This technique was used by Huebener in his size effect work on gold³¹.

Figure 9. Temperature History Schematic

A. Water-To-Methanol Quench

1. Ice And Water Quench (1st Stage)
2. Transfer Time
3. Dry Ice And Methanol Quench (2nd Stage)
4. Assembly Time
5. Liquid Nitrogen Quench (3rd Stage)

B. Methanol Quench

6. Methanol Quench
7. Assembly Time
8. Liquid Nitrogen Quench

The measurement is performed with the lower junction in a liquid nitrogen bath and the upper junction at room temperature. No clamping was required.

The time from quench to insertion of both hot and cold junctions into a liquid nitrogen bath was < 15 seconds. Hence vacancy loss resulting from vacancies annealing out to sinks was minimal. After the specimen had reached thermal equilibrium and after assembly the specimen was inserted into the cryostat. The resistance of both the specimen and the well-annealed wire were then measured at 4.2°K . This measurement was needed for obtaining the quenched-in resistivity. Then the specimen was reinserted into a liquid nitrogen bath with both the upper and lower junctions immersed.

In order to perform the measurement itself the specimen was raised so that the upper junction was in air and the lower junction was in liquid nitrogen. As the upper junction warmed to room temperature the voltage signal on the X-Y recorder increased until a maximum was reached. Then due to vacancy loss in the upper part of the specimen the voltage signal began to decrease. The value of ΔS used was the maximum signal extrapolated back to zero time, i.e. the time when the upper junction was removed from the liquid nitrogen bath.

This measurement has the advantage that it is possible to rapidly cool the specimen immediately after quench. The disadvantage is that one has no control over the temperature gradient and only one value of temperature difference is obtainable.

J. Determination Of Vacancy Concentration

The resistance of the specimen and well-annealed wire were measured at 4.2 °K. These measurements were identical to the room temperature resistance measurement described in Section H Paragraph 2. First the resistance ratio of the specimen and well-annealed wire were obtained; then the resistivities of both of these wires were computed at 4.2 °K using the value of resistivity of aluminum at room temperature from Simmons and Balluffi¹¹. The quenched-in resistivity due to vacancies was calculated by subtracting the resistivity of the well-annealed wire from the specimen resistivity. Finally the vacancy concentration was determined using the Simmons and Balluffi value¹¹ for the intrinsic resistivity of a vacancy in aluminum as 3×10^{-6} ohm-cms/at. % .

K. Temperature Measurement

Two thermocouples (see Fig. 10) were used: one to measure the temperature of the hot junction and one to

Figure 10. Hot Junction
Thermometer Arrangement

measure the temperature of the heat sink junction.

The thermocouple wire used was obtained from the Sigmund-Cohn Corporation. One wire material was 0.003 in. in diameter teflon coated gold + 0.07 at % iron. The other was 0.003 in. in diameter teflon coated chromel. The two .003 in wires were spot-welded together and to a 0.0005 in copper foil, 0.5 cms by 1 cm. The junction and foil were thermally insulated from the sample holder by a phenolic wafer. Good thermal contact with the aluminum wire junction was aided by a coating of Apiezon N or Dow-Corning high vacuum grease. These thermocouple materials have been calibrated by the National Bureau of Standards of Boulder, Colorado³² and their published calibrations were used.

It was necessary to use the small diameter thermocouple wires and the thin foils to ensure that the thermocouple mass was small compared to the mass of the specimen wire with which it was in contact. Hence very little heat was dissipated from the specimen wire by the thermocouple so that the temperature gradient along the specimen wire was not significantly disturbed³³.

The drift of the sink temperature was 1 °K at a gradient of 80 °K.

L. Temperature Control And Heat Transfer Considerations

1. Temperature Controller: The circuit, shown in Fig. 11, was used to very slowly change the current

Figure 11. Temperature Controller

to the heater element. The change of current was reasonably linear with time. This was achieved by picking off the voltage from a motor driven potentiometer. The requirements for the experiment were that the heating current be such that a wide temperature range was spanned within a few hours since the liquid helium boil-off rate limits the time available for measurement. The controller produced a temperature change from 4.2 °K to 77 °K over a period of 5½ hours.

2. Heat Transfer Considerations: In this experiment it was important to control the heat flow at the hot junction so that a wide range of temperature could be spanned while at the same time maintaining the cold junction temperature at the temperature of the cryogenic liquid. This had to be done efficiently so that a minimum of liquid helium was boiled off.

The mechanisms of heat transfer determined how efficiently the above goal could be achieved. Heat is transferred by (1) gas conduction, (2) solid conduction and (3) radiation.

For the pressures achieved with the apparatus (< 1 millitorr) and the cryogenic temperatures involved, the dominant heat transfer mechanism was solid conduction. Calculations indicate that the dominant path for heat transfer was through the aluminum wires since pure aluminum

has a very high thermal conductivity. Thus the wire diameter and the wire span became very important. For example, .018 in. diameter wires could not be used due to the excessive liquid helium boil-off.

The structural materials used in the sample holder were to a large extent determined by heat transfer considerations. It was desired to have little heat transfer through the structural support tubes; hence thin-wall stainless steel tubing was used. Phenolic was used where high thermal resistance and electrical insulation was required. Copper was used for low thermal resistance. Emerson and Cuming 2850-GT Stycast gave coatings which had a low thermal resistance but a high electrical resistance and were unaffected by methanol.

IV. RESULTS AND ANALYSIS

A. Thermoelectric Voltage Curves

The thermoelectric voltage between the well-annealed wire and the specimen wire containing vacancies was measured as a function of hot junction temperature. The cold junction was held at a constant temperature by the heat sink plate which was thermally connected to the bath. For hot junction temperatures between 4.2 °K and 77 °K the bath in which the copper can was immersed was liquid helium. For temperatures between 77 °K and 150 °K the bath was liquid nitrogen. The absolute value of voltage is not significant since it is measured relative to the temperature of the cold junction. For clarity a constant voltage has been added to the liquid nitrogen bath data matching it with the liquid helium bath data. The measured thermoelectric voltage curves for the water-to-methanol quench are shown in Figs. 12-17.

B. Thermopower Curves For Water-To-Methanol Quench

The difference in thermopower between the well-annealed wire and the specimen wire containing vacancies was then found by taking the temperature derivative of the thermoelectric voltage curves. See Figs. 18-23, solid lines. The main characteristic of these curves is the pronounced negative minimum which occurs at approximately 30 °K. A

second feature is the small broad positive maximum which occurs at approximately 90°K . Thus the thermopower curves exhibit a double-humped shape. This shape is very similar to the dilute alloy curves in aluminum obtained by Huebener¹, except that the negative peak is much enhanced relative to the positive peak in the vacancy data.

The dashed curves represent the theoretical electron-diffusion thermopower as computed from the Nielsen-Taylor theory. This calculation was discussed in Chapter II Section C. Note the good agreement of the negative peak magnitudes and the location in temperature, especially for the high concentrations.

For the samples the resistance purity ratio $R_{295^{\circ}\text{K}}/R_{4.2^{\circ}\text{K}}$, was measured to be from 1900 to 2400.

C. Thermopower Curves For Methanol Quench

See Figs. 24-28. In the temperature region 4.2°K to 77°K , these curves are generally the same as in the water-to-methanol quench. Again the negative minimum occurs at approximately 30°K . The maximum concentration achieved is much lower, and the magnitude of the negative minimum is correspondingly lower than in the methanol-to-water quench.

In the temperature region, 77°K to 150°K , the curves show a similar behaviour for the two lowest quench temperatures but a highly anomalous behaviour for the higher quench temperatures, especially for $T_Q = 462^{\circ}\text{C}$.

Figure 12. Thermoelectric Voltage Curve

For Vacancies In Aluminum

$$T_Q = 330^{\circ}\text{C}$$

Water-To-Methanol Quench

Concentration, $c = 0.033 \times 10^{-3}$ at. %

Figure 13. Thermoelectric Voltage Curve

For Vacancies In Aluminum

$$T_Q = 416^{\circ}\text{C}$$

Water-To-Methanol Quench

Concentration, $c = 0.852 \times 10^{-3}$ at. %

Figure 14. Thermoelectric Voltage Curve

For Vacancies In Aluminum

$$T_Q = 476 \text{ }^{\circ}\text{C}$$

Water-To-Methanol Quench

Concentration, $c = 1.94 \times 10^{-3}$ at. %

Figure 15. Thermoelectric Voltage Curve

For Vacancies In Aluminum

$$T_Q = 538^{\circ}\text{C}$$

Water-To-Methanol Quench

Concentration, $c = 2.36 \times 10^{-3}$ at. %

Figure 16. Thermoelectric Voltage Curve

For Vacancies In Aluminum

$T_Q = 585^\circ\text{C}$

Water-To-Methanol Quench

Concentration, $c = 3.05 \times 10^{-3}$ at. %

Figure 17. Thermoelectric Voltage Curve

For Vacancies In Aluminum

$$T_Q = 555^{\circ}\text{C}$$

Water-To-Methanol Quench

Concentration, $c = 3.48 \times 10^{-3}$ at. %

Figure 18. Thermopower Curve For
Vacancies In Aluminum

$$T_Q = 330^\circ\text{C}$$

Water-To-Methanol Quench

Concentration, $c = 0.033 \times 10^{-3}$ at. %

Figure 19. Thermopower Curve For
Vacancies In Aluminum

$$T_Q = 416^{\circ}\text{C}$$

Water-To-Methanol Quench

Concentration, $c = 0.852 \times 10^{-3}$ at. %

Figure 20. Thermopower Curve For

Vacancies In Aluminum

$$T_Q = 476^\circ\text{C}$$

Water-To-Methanol Quench

Concentration, $c = 1.94 \times 10^{-3}$ at. %

Figure 21. Thermopower Curve For
Vacancies In Aluminum

$$T_Q = 538^{\circ}\text{C}$$

Water-To-Methanol Quench

Concentration, $c = 2.36 \times 10^{-3}$ at. %

Figure 22. Thermopower Curve For
Vacancies In Aluminum

$$T_Q = 585^\circ\text{C}$$

Water-To-Methanol Quench

Concentration, $c = 3.05 \times 10^{-3}$ at. %

Figure 23. Thermopower Curve For
Vacancies In Aluminum

$$T_Q = 555\text{ }^{\circ}\text{C}$$

Water-To-Methanol Quench

Concentration, $c = 3.48 \times 10^{-3}$ at. %

Figure 24. Thermopower Curve For
Vacancies In Aluminum

$$T_Q = 365^\circ\text{C}$$

Methanol Quench

Concentration, $c = 0.23 \times 10^{-3}$ at. %

Figure 25. Thermopower Curve For
Vacancies In Aluminum

$$T_Q = 421^\circ\text{C}$$

Methanol Quench

Concentration, $c = 0.38 \times 10^{-3}$ at. %

Figure 26. Thermopower Curve For
Vacancies In Aluminum

$$T_Q = 462^\circ\text{C}$$

Methanol Quench

Concentration, $c = 0.87 \times 10^{-3}$ at. %

Figure 27. Thermopower Curve For
Vacancies In Aluminum

$$T_Q = 508^\circ\text{C}$$

Methanol Quench

Concentration, $c = 0.85 \times 10^{-3}$ at. %

Figure 28. Thermopower Curve For
Vacancies In Aluminum

$$T_Q = 577^\circ\text{C}$$

Methanol Quench

Concentration, $c = 0.88 \times 10^{-3}$ at. %

The resistance purity ratio, $R_{295^{\circ}\text{K}}/R_{4.2^{\circ}\text{K}}$ was measured to be from 1900 to 3100.

D. Separation Of The Thermopower Components, Method I

The change in electron-diffusion thermopower, ΔS_e , determined by Method I is shown in Fig. 29 for appropriate vacancy concentrations. (See Chapter II Section B for theoretical development). Note that these curves are positive at all temperatures and peak at approximately 30°K . The value used for S_e^0/T was taken from Gripshover, VanZytveld and Bass³⁴ as

$$S_e^0/T = -3.0 \times 10^{-3} \text{ } \mu\text{V}/(^{\circ}\text{K})^2 \quad (49)$$

The value of H (defined in Eq. 12) was evaluated from the data at $T = 150^{\circ}\text{K}$. The values of ΔS at 150°K and $\Delta\rho$ which were used to calculate each curve in Fig. 29 are listed in Table I. These data correspond to that obtained in the water-to-methanol quench for each particular quench temperature.

Since now both ΔS and ΔS_e are known by applying Eq. (2), one obtains the curves for the phonon drag component shown in Fig. 30.

Figure 29. Electron-Diffusion Component Of The Change
In Thermopower For Vacancies In Aluminum
Water-To-Methanol Quench: Method I

Curve No.	T_Q (°C)	Concentration, $c \times 10^3$ at. %
1	416	0.85
2	476	1.94
3	538	2.36
4	585	3.05
5	555	3.48

Figure 30. Phonon Drag Component Of The Change In
Thermopower For Vacancies In Aluminum
Water-To-Methanol Quench: Method I

Curve No.	T_Q	Concentration, $c \times 10^3$
	(°C)	at. %
1	416	0.85
2	476	1.94
3	538	2.36
4	585	3.05
5	555	3.48

TABLE I

Curve No. On Fig. 29	Total Measured Thermopower, ΔS $10^{-9} \text{ v/}^\circ\text{K}$	Quenched-In Resistivity, $\Delta \rho$ $10^{-9} \Omega \text{cms}$
1	3.2	2.56
2	6.0	5.83
3	8.5	7.07
4	9.5	9.15
5	10.2	10.45

E. Evaluation Of The Rayleigh Scattering Parameter

Utilizing the expression for the lattice thermal conductivity, K_L in Eq. (33) and the expression for the inverse phonon scattering relaxation time, τ_0^{-1} in Eq. (35), the constants b and β were evaluated. The value used for the velocity of sound v_s was ³⁵,

$$v_s = 6.42 \times 10^5 \text{ cms/sec} . \quad (50)$$

The Debye temperature, θ was taken to be 428°K . The value for the lattice thermal conductivity, K_L , was taken from White's table ³⁶ as,

$$K_L = 19/T \pm 50\% \text{ ergs cm}^{-1} \text{sec}^{-1} \text{ }^\circ\text{K}^{-1} . \quad (51)$$

The results are

$$b = 4.0 \times 10^{-8} \text{ sec/degree and } \beta = 62^\circ \text{K} . \quad (52)$$

Next, the constant A was determined in the expression for S_g^0 (Eq. 36). The value used for S_g^0 was taken from the graph of Gripshover, VanZytveld and Bass³⁴ at 100°K as $-2.16 \mu\text{V}/^\circ\text{K}$; see Fig. 2. The value of A determined is,

$$A = -.40 \mu\text{V}/^\circ\text{K} . \quad (53)$$

At this point in order to determine the scattering parameter, a, from Eq. (39), an experimental value of ΔS_g is needed. These values were obtained using Methods I and II as described in the theory at 100°K . These scattering parameters, a, obtained are listed in Table II.

It is worthwhile to compare these experimental values with the values obtained from the theories of Klemens and Carruthers (see Chapter II Section D). Using the atomic volume of the crystal for aluminum as $16.53 \times 10^{-24} \text{ cms}^3$, then from Eq. (40)

$$a/c = 6.0 \times 10^{-43} \text{ L}^2 \text{ sec}^3 / \text{at } \% . \quad (54)$$

In Klemen's theory the expression for L^2 is given by Eq. (41). Klemens states that for vacancies $\Delta M/M = -1$, $\Delta F/F = -1$ and $Q = 3.2$ From White³⁶, $\gamma = 2.35$.

It is also necessary to obtain the relative change in the nearest neighbor distance, $\Delta R/R$. From Butcher, Hutto and Ruoff⁸, the activation volume of a vacancy is $\Delta V = 22 \times 10^{-24} \text{ cms}^3$. The radius of a vacancy is then $(\Delta V)^{1/3} = 2.80 \times 10^{-8} \text{ cms}$. The atomic volume for an aluminum ion, ΔV_{Al} is taken from Kittel²³ as 16.95×10^{-24} so that $(\Delta V_{Al})^{1/3} = 2.57 \times 10^{-8} \text{ cms}$. Using Klemens' method one obtains $\Delta R/R = + .041$. L^2 can now be calculated; one obtains $L^2 = .52$. Then from Klemens' theory one obtains $a/c = 3.1 \times 10^{-43} \text{ sec}^3/\text{at.}\%$. From Carruthers' theory, using Eq. (42) one obtains $a/c = 4.4 \times 10^{-43} \text{ sec}^3/\text{at.}\%$.

The values calculated for a by each of the two methods for each quench temperature of the water-to-methanol procedure are shown in Table II.

TABLE II

Quench Temperature $T_Q - (^{\circ}\text{C})$	$a/c \times 10^{43}$ $\text{sec}^3/\text{at.}\%$	
	Method I	Method II
416	0.3	16.4
476	2.0	18.7
538	3.4	20.3
585	2.9	19.9
555	1.1	18.3

It should be noted that if this procedure were applied to the negative minimum in the thermopower data, it would give a negative value of the scattering parameter which is non-physical. This implies that the negative minimum can not be explained as being due to phonon drag by any simple theory.

The change in phonon drag thermopower as determined from experiment using Methods I and II is shown in Figs. 31 and 32, respectively. The temperature dependence of the theoretical expression for ΔS_g obtained from Eq. (39) has been evaluated and also has been plotted on Figs. 31 and 32 (dashed lines) for comparison purposes. These theoretical values have been normalized to the experimental values at 100 °K.

F. Intrinsic Thermopower Of A Vacancy In Aluminum

If it can be shown to be true that at 150 °K, ΔS is solely due to the electron-diffusion component and if only monovacancies are present, then from the slope of Fig. 33 the intrinsic thermopower of a lattice vacancy in aluminum is $(\Delta S_e/c)_{150^\circ K} = 3.3 \pm .5 \mu V/^\circ K$ at. %. Then for 1 at.% of vacancies, $S_e^i = 3.3 \pm .5 \mu V/^\circ K$, and from Eq. (8), $\left[\frac{\partial \ln \Delta \rho}{\partial \ln \epsilon} \right]_\zeta$ can be calculated to be 10.4 .

**Figure 31. Change In Phonon Drag Thermopower Temperature
Dependence Curves: Method I**
**Solid Lines Are Determined From Experiment
By Method I**
Dashed Lines Are Computed From Eq. (39)

Figure 32. Change In Phonon Drag Thermopower Temperature
Dependence Curves: Method II
Solid Lines Are Determined From Experiment
By Method II
Dashed Lines Are Computed From Eq. (39)

Figure 33. Change In Thermopower Of Aluminum At
150 °K Versus Quenched-In Vacancy
Concentration

G. Plots Of $\ln\Delta S$ And $\ln\Delta\rho$ Versus $1/T$

From the $\Delta\rho$ plot (see Fig. 34) for the water-to-methanol quench for $T_Q > 475^\circ\text{C}$ a slope of $3.7 \times 10^3^\circ\text{C}$ is obtained and for $T_Q < 475^\circ\text{C}$ the slope is consistent with that obtained by Bass whose data is shown for comparison purposes. From his data a slope of 6.4×10^3 is obtained for $T_Q > 475^\circ\text{C}$ and a slope of 7.7×10^3 is found for $T_Q < 475^\circ\text{C}$ which results in $E_f = 0.66$ eV. The ΔS plot (see Fig. 35) has the same slopes, however the break point occurs at 415°C .

The $\Delta\rho$ curve (see Fig. 36) for the methanol quench is only linear to near 450°C and then reaches a saturation value for $\Delta\rho$ which is about $2.6 \times 10^{-9} \Omega\text{cms}$. Note that the ΔS curve (see Fig. 37) for the methanol quench is very unusual. At $T_Q = 462^\circ\text{C}$, one obtains $\Delta S/c = 61 \mu\text{V}/^\circ\text{K}$ at. %, an anomalously high value.

Figure 34. Semi-Logarithmic Plot Of The Quenched-In
Resistivity, $\Delta\rho$ Versus The Reciprocal
Temperature, $1/T$
Water-To-Methanol Quench

Figure 35. Semi-Logarithmic Plot Of The Change In
Thermopower Due To Vacancies, ΔS Versus
The Reciprocal Temperature, $1/T$
Water-To-Methanol Quench

Figure 36. Semi-Logarithmic Plot Of The Quenched-In
Resistivity, $\Delta\rho$ Versus The Reciprocal
Temperature, $1/T$
Methanol Quench

Figure 37. Semi-Logarithmic Plot Of The Change In
Thermopower Due to Vacancies, ΔS , Versus
The Reciprocal Temperature, $1/T$
Methanol Quench

V. DISCUSSION AND CONCLUSION

A. Discussion Of Results Based On Method I

The analysis of the data based on Method I is in keeping with the commonly accepted theory of electron-diffusion thermopower. Its use creates a major difficulty in interpretation of the data presented here because it implies that vacancies enhance the phonon drag thermopower of aluminum. No theory of phonon drag formulated to date will predict this enhancement, although a possible explanation has been suggested by Huebener to explain the same problem in alloys of aluminum. His hypothesis is that this enhancement could be due to anisotropy of the electron scattering as described in Chapter I. A quantitative prediction of enhancement, however, is not yet possible by this mechanism.

B. Discussion Of Results Based On Method II

The following interpretation of the double-humped curve of thermopower of vacancies is proposed. The negative minimum at 30 °K is due to the electron-diffusion thermopower and the positive maximum near 85 °K is due to the phonon drag thermopower. This is shown schematically in Fig. 38.

This work provides evidence that the negative minimum in the vacancy thermopower curve is due to the

**Figure 38. Proposed Resolution Of The Total Change
In Thermopower Into The Electron-Diffusion
And Phonon Drag Components**

- A. Shows Schematically The Double-Humped
Form Of The ΔS Curve**
- B. Shows Schematically The Proposed Curves
Of The Thermopower Components, ΔS_e and
 ΔS_g**

electron-diffusion component. It is apparent, in fact, from Figs. 19-23 that the Nielsen-Taylor theory predicts a negative minimum of the same magnitude and occurring at the same temperature as the experimentally obtained curves. This successful prediction of the peak temperature was also found by Dudenhoeffer and Bourassa⁵ in the case of aluminum alloys. The concentration spanned by the vacancy data and the alloy data is from 0.33×10^{-4} at % to 0.5 at.% .

There is also evidence that the positive maximum in ΔS is the expected reduction of the phonon drag component of thermopower due to the vacancies. This evidence applies both to Method I and Method II and comes from the calculation of the Rayleigh scattering parameter a . The experimental determination of this parameter gives values consistent with the values calculated from the theoretical expressions of Klemens²¹ and Carruthers²². In addition the temperature dependence of the change in phonon drag thermopower due to vacancies in aluminum has been calculated using the theoretical expressions of Huebener¹². The agreement with the experimental data is excellent. Therefore, this supplies more evidence that the phonon drag component is significant in this temperature range. These calculations were also made on two of the alloy curves of Huebener¹ and the results are consistent with the proposed explanation.

C. Discussion Of Formation Energy Results

1. Water-To-Methanol Quench: The monovacancy formation energy, E_f , obtained from plots of ΔS and $\Delta\rho$ are consistent with Bass' data below $T_Q = 475^\circ\text{C}$ but the slope is lower than Bass' above $T_Q = 475^\circ\text{C}$. This was expected because Bass used a brine quench medium which gives a somewhat higher quench rate ($6 \times 10^4^\circ\text{C/sec}$). The slightly lower quench rate in this experiment ($2.5 \times 10^4^\circ\text{C/sec}$) causes a higher vacancy loss at high temperatures. Brine has a high electrical conductivity and was not used in this experiment.

2. Methanol Quench: The $\Delta\rho$ plot exhibits the expected behavior of the slower quenching rates in aluminum, i.e. the plot is linear at the low quench temperatures but reaches a saturation value and remains constant for the higher quench temperatures²⁸. However, the ΔS plot is anomalous and appears to have a maximum around $T_Q = 460^\circ\text{C}$. The formation of vacancy clusters during the quench is proposed as a possible explanation for this maximum. ΔS may be different for each type of cluster. This plot demonstrates the sensitivity of ΔS to the type of scattering center in contrast with $\Delta\rho$.

D. The Intrinsic Thermopower Of Monovacancies In Aluminum

In Chapter IV Section G, a value for $\Delta S/c$ for monovacancies for the water-to-methanol quench is given.

The value of $\Delta S/c$ (Method I) = $3.3 \mu V/^{\circ}K$ at. % . Method I was used to calculate ΔS_e with the stipulation that two conditions be met. The first condition was that only monovacancies were present. This condition may not be true because other experiments^{6,7,8,11} indicate a large percentage of divacancies may be present in equilibrium at high temperatures. The error in the value of $\Delta S/c$ due to a divacancy contribution, however, is within the experimental error of the data.

The second condition was that at $150^{\circ}K$ all of ΔS was due to the electron-diffusion component, ΔS_e . Using Method II to calculate ΔS_e indicates that there may be a considerable amount of residual phonon drag component at $150^{\circ}K$. Method II gives a value for ΔS_e which is slightly negative and in fact,
 $\Delta S_e/c$ (Method II) = $-4.1 \mu V/^{\circ}K$ at. % .

It is clear that the intrinsic thermopower of a monovacancy in aluminum can not be uniquely specified until the amount of phonon drag present is known.

E. Sources Of Error

There was a background drift of up to $0.1 \mu V$ over a period of a few hours at $77^{\circ}K$ and above. This drift was attributed to changing environmental conditions. Long term temperature drifts can cause temperature gradients which

can produce considerable scatter in the data. The room temperature varied from 20 °C to 25 °C.

There was a variation in temperature along the specimen length during the anneal. The accuracy of the quench temperature measurement is estimated to be ± 5 °C. The maximum change of hot junction temperature with time was 1 °K per minute. The error in the hot junction temperature measurement due to this non-equilibrium situation was found to be negligible.

A different specimen was made up for each run. The effect for ΔS due to variations from sample to sample taken from the same spool are difficult to estimate. Variations in the quench from run to run due to such factors as quench rate, variations in the room temperature annealing time, and amount of cold working of the specimen, probably contribute to a large percentage of the scatter. Systematic errors due to inherent instability in the amplifier systems are estimated to be 2% of the maximum change in thermopower.

Variations from 1900 to 2400 occurred in the purity ratio, i.e. the resistance ratio of the well-annealed wire, $R_{295^\circ\text{K}}/R_{4.2^\circ\text{K}}$. This represented a change of $\pm 12\%$ in the calculated well-annealed resistivity at 4.2 °K. Since the quenched-in resistivity $\Delta\rho$ is the difference of the two resistivities of nearly the same value especially for low

concentrations, the error produced in $\Delta\rho$ from variations in purity ratio is large.

From the scatter of the data in the water-to-methanol quench, the thermoelectric voltage error estimation is $\pm 20\%$ at 30°K and $\pm 6\%$ at 150°K for the lowest concentration, and is $\pm 1\%$ at 30°K and $\pm 2\%$ at 150°K for the highest concentration. For the highest concentration, the thermopower error estimation is $\pm 5\%$ at 30°K and $\pm 10\%$ at 150°K . From the scatter of the data in the semi-logarithmic plots, the error in ΔS and $\Delta\rho$ is estimated as $\pm 10\%$ for the highest quench temperature.

The scatter in the thermopower curves for the methanol quench is greater than it is in the water-to-methanol quench particularly for the liquid nitrogen bath data. As this was an earlier series of experiments, the instrumentation was not as good as in the later water-to-methanol quench series. Hence, the accuracy is not expected to be as good.

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