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Thermoelectric Power of Aluminum and Dilute Aluminum Alloys[*]

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The thermoelectric power of dilute alloys of aluminum with Ag, Zn, Mg, and Au has been measured versus pure aluminum between 4.2 and 460°K. The solute concentrations were in general 0.1 at.% or smaller. The absolute thermopower of high-purity Al has been measured between 4.2 and 300°K. The phonon-drag component S^g in Al is negative, with a peak at about 70°K. At temperatures above 40 to 80°K, depending on the composition, the alloys show the usual reduction in the phonon-drag thermopower. However, at lower temperatures, an increase in $|S^g|$ due to alloying is observed in all specimens. It is suggested that this anomaly in the phonon-drag thermopower of the dilute aluminum alloys is because of the anisotropy of the electron scattering. The results can be explained with a relaxation time for electron-phonon scattering which is shorter in the third band than in the main portion of the Fermi surface, in combination with an isotropic electron-impurity interaction. The electron diffusion component S^e in Al is negative. All alloys show a positive change in S^e.

I. INTRODUCTION

At not too high temperatures, the thermoelectric power S of a pure metal consists in general of two components: the electron-diffusion component S^e and the phonon-drag component S^g. The contribution S^e is caused by the deviation of the *electron system* from the equilibrium distribution in the presence of a temperature gradient. The component S^g is due to the deviation of the *phonon system* from the equilibrium distribution in the presence of a temperature gradient in combination with the electron-phonon interaction. The introduction of impurities into a metal causes a change of both quantities S^e and S^g. 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 in general *reduced* because of the presence of impurities, simply because the additional phonon scattering by the impurities reduces the phonon current set up by the temperature gradient. At low temperatures, this reduction of S^g is rather small since the phonon scattering cross section of point defects decreases strongly with decreasing phonon frequency. An exception to this rule may occur if the phonon scattering by point defects shows a resonance at low phonon frequencies. The resonant scattering of phonons by point defects has been investigated extensively through lattice heat-conductivity measurements in electrical insulators.[1] The effect of quenched-in lattice vacancies on the thermoelectric power of platinum has been explained recently[2] by a low-frequency resonance in the phonon scattering cross section of vacancies. Resonance modes associated with substitutional atoms can exist if the force constants of the foreign atom are very small, or if the mass is very large relative to the host atoms. Part of the present study of the thermoelectric power in dilute aluminum alloys was stimulated by the desire to look at the change in the phonon-drag thermopower caused by a heavy impurity in a light host crystal. Measurements with dilute aluminum-silver alloys were particularly interesting, since here the existence of a low-frequency resonance mode has been detected recently[3,4] through the enhancement of the low-temperature lattice heat capacity.

Van Baarle,[5] Bailyn,[6] and Dugdale and Bailyn[7] have shown recently, that anomalies in the low-temperature phonon-drag thermopower in impure systems can occur if the relaxation time τ_i for the electron scattering by the impurities and the relaxation time τ_{ph} for the electron scattering by phonons vary differently over the Fermi surface. The difference in the anisotropy of τ_i and τ_{ph} can lead at low temperatures to the surprising result that the absolute magnitude of S^g is enhanced or that S^g changes its sign because of alloying. An enhancement of $|S^g|$ at low temperatures has been reported recently for dilute silver-gold,[5,8] silver-antimony,[5] and nickel-copper[9] alloys. A reversal in sign of S^g, because of alloying, has been found in dilute gold-platinum alloys.[10,11] A rather complete discussion of these anomalies in the noble metals has been given by Dugdale and Bailyn.[7]

In view of the anomalies in the low-temperature phonon-drag thermopower of dilute alloys, discussed above, we measured the thermopower of aluminum and a series of dilute aluminum alloys between 4.2 and

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[*] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[1] A. A. Maradudin, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 18, p. 274.

[2] R. P. Huebener, Phys. Rev. 146, 490 (1966).

[3] H. Culbert and R. P. Huebener, Phys. Letters 24A, 530 (1967).

[4] H. Culbert and R. P. Huebener, in *Proceedings of the International Conference on Localized Excitations in Solids, 1967* (Plenum Press, Inc., New York, 1968).

[5] C. Van Baarle, Physica 33, 424 (1967).

[6] M. Bailyn, Phys. Rev. 157, 480 (1967).

[7] J. S. Dugdale and M. Bailyn, Phys. Rev. 157, 485 (1967).

[8] A. M. Guenault, Phil. Mag. 133, 17 (1967).

[9] T. Farrell and D. Greig, in *Proceedings of the Tenth International Conference on Low-Temperature Physics, Moscow, 1966* (Proizvodstrenno-Izdatel'skii Kombinat, VINITI, Moscow, 1967).

[10] R. P. Huebener and C. Van Baarle, Phys. Letters 23, 189 (1966).

[11] R. P. Huebener and C. Van Baarle, Phys. Rev. 159, 564 (1967).

460°K. Aluminum has the advantage that it can be purified relatively easily. Apparently, the low-temperature thermopower of aluminum[12] is not seriously affected by traces of magnetic impurities, which dominate quite often the low-temperature behavior in "high-purity" noble metals.[13] The alloys investigated were aluminum-silver, aluminum-zinc, aluminum- magnesium, and aluminum-gold. The solute concentrations were 0.1 at.% or smaller except for the Al-Mg alloy. Preliminary results were reported earlier.[14]

II. EXPERIMENTAL PROCEDURE

The specimen material was polycrystalline wire of 0.25 mm diam.[15] The aluminum wire was drawn from 99.9999% pure material. The alloy wires were made from 99.9999% pure Al and 99.999% pure solute material. The various specimen wires, including their source, are listed in Table I. Before mounting the sample wires, they were placed for 3 to 5 min in an aqueous solution of NaOH and were rinsed with distilled water. After mounting the specimens on a sample holder, they were rinsed in acetone and methyl alcohol. Then the specimen wires were annealed in air at elevated temperatures by passing direct current through them and were gradually cooled to room temperature. The annealing schedule for the various samples was as follows: pure Al: about 16 h at 450°C; Al-Ag alloys: about 16 h at 500°C; Al-Zn alloys: about 4 h at 260°C; Al-Mg alloys: about 20 h at 400°C; Al-Au alloy: about 16 h at 550°C. The annealed aluminum wires had a resistance ratio $R(293°\text{K})/R(4.2°\text{K})$ between 2200 and 2800. The specimen arrangement and the technique of the thermoelectric measurements were similar to those described elsewhere.[2,13] The absolute thermoelectric power of pure aluminum was obtained from measurements versus 99.9999% pure lead.[16] For the absolute thermopower of Pb the data of Borelius *et al.*[17] and of Christian *et al.*[18] were used. The aluminum alloys were always measured versus pure aluminum.

TABLE I. Composition and source of the specimens. $\Delta\rho$ is the electrical resistivity difference between the alloy and pure Al at 4.2°K. ΔS is the thermopower of the alloy versus pure Al at 453°K.

Sample	Admixture	Source	$\Delta\rho$ ($10^{-8}\ \Omega$ cm)	ΔS(453°K) ($10^{-2}\ \mu$V/°K)
1	pure	C.A.	...	...
3	0.03 at.% Ag	S.C.	3,33	1,73
10	0.10 at.% Ag	C.A.	11.7	4,89
4	0.03 at.% Zn	S.C.	0.74	0.78
9	0.10 at.% Zn	S.C.	2.18	2.20
11	0.10 at.% Zn	C.A.	2.26	2.20
12	0.10 at.% Mg	C.A.	3,36	1,28
13	0.50 at.% Mg	C.A.	20,5	7.5
2	0.03 at.% Au	S.C.	0.268	...

Because of the difficulties one encounters in spot welding aluminum, electrical contact between both wires of the sample thermocouple at the hot and the cold junction was made by the mechanical pressure supplied by the nylon block carrying the thermometer and the copper plate at the heat sink. The potential lead wires of the specimens, which were always the pure Al wires, were spot welded to extensions of annealed aluminum wires (99.9999% pure) leading out of the cryostat into a thermally shielded oil bath kept at room temperature. Within the oil bath, the aluminum wire was connected to copper wire leading to the potentiometer. Below 77°K, the temperature of the hot junction was measured with a germanium resistance thermometer.[19] Between 77°K and room temperature, an Au-2.1% Co versus Cu thermocouple was used.

Above 273°K, the change ΔS due to alloying was measured in the following way. From the annealed alloy wire and two annealed aluminum wires a thermocouple was made by spot welding. The distance between both junctions was about 30 cm. One junction was then placed in an ice-water bath. The other junction was placed in a stirred oil bath which was heated up to 185°C. The temperature of the oil bath was raised by 0.3°C per min. The temperature of the oil bath was measured with a copper-constantan thermocouple.

The data were taken at temperature intervals of about 0.3°K below 10°K, about 0.8°K between 10 and 80°K, and 1–2°K above 80°K. The thermoelectric power was obtained by differentiating the emf versus temperature curves with respect to the temperature using a CDC 3600 computer. A second-order polynomial was fitted by the method of least squares to either 5, 7, or 9 neighboring points. Then the derivative was calculated for the center point. By shifting the cluster of neighboring points one step at a time, the thermopower was obtained as a function of temperature.

III. DATA ANALYSIS

We collect in the following the expressions which describe the thermoelectric power as a function of temperature, and which indicate how the electron diffusion component and the phonon-drag component can be separated from each other. The absolute thermopower S_0 of a pure metal is the sum of the electron diffusion component $S_0{}^e$ and the phonon-drag component $S_0{}^g$,

$$S_0 = S_0{}^e + S_0{}^g. \tag{1}$$

The electron diffusion component $S_0{}^e$ is in first approxi-

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[12] A. R. De Vroomen, C. Van Baarle, and A. J. Cuelenaere, Physica **26**, 19 (1960).

[13] R. P. Huebener, Phys. Rev. **135**, A1281 (1964).

[14] R. P. Huebener, Bull. Am. Phys. Soc. **12**, 533 (1967).

[15] Obtained from Cominco American, Inc., Spokane, Wash., and from Sigmund Cohn, Inc., Mount Vernon, N. Y.

[16] Obtained from Cominco American, Inc., Spokane, Wash.

[17] G. Borelius, W. H. Keesom, C. H. Johansson, and J. O. Linde, Proc. Acad. Sci. Amsterdam **35**, 10 (1932).

[18] J. W. Christian, J. P. Jan, W. B. Pearson, and I. M. Templeton, Proc. Roy. Soc. (London) **A245**, 213 (1958).

[19] Obtained from Honeywell, Inc., Philadelphia, Pa.

mation given by

$$S_0^e = \frac{\pi^2 k_B^2 T}{3e}\left[\frac{\partial \ln\rho_0(E)}{\partial E}\right]_{E_F}. \tag{2}$$

Here k_B is Boltzmann's constant, T the absolute temperature, and e the absolute value of the elementary charge; ρ_0 is the electrical resistivity. E is the energy of the conduction electrons and E_F the Fermi energy. The phonon-drag component S_0^g can be written approximately as[20]

$$S_0^g = AT^3\int_0^{\Theta/T} dz\, \frac{z^4 e^z}{(e^z-1)^2}\alpha(z). \tag{3}$$

Here A is a constant, Θ the Debye temperature, and $z=\hbar\omega/k_BT$ ($\hbar$ = Planck's constant divided by 2π, ω = phonon frequency). The function $\alpha(z)$ is the relative probability for the phonon with the frequency ω to interact with an electron.

The change ΔS due to point defects, which scatter electrons and phonons, is given by

$$\Delta S = \Delta S^e + \Delta S^g, \tag{4}$$

with[21]

$$\Delta S^e \equiv S^e - S_0^e = \frac{S_0^e}{W_0^e/\Delta W^e+1}\left[\frac{\partial \ln\Delta\rho/\partial E}{\partial \ln\rho_0/\partial E}-1\right]_{E_F} \tag{5}$$

and

$$\Delta S^g \equiv S^g - S_0^g \approx -AT^3\int_0^{\Theta/T} dz \times \frac{z^4 e^z}{(e^z-1)^2}\,\frac{\alpha(z)}{1+\tau_i(z)/\tau_0(z)}. \tag{6}$$

Here S^e and S^g are the electron diffusion component and the phonon-drag component, respectively, in the impure system. W_0^e is the electronic thermal resistivity of the pure metal. $\Delta\rho$ and ΔW^e are the additional resistivities due to the impurity admixture. τ_i and τ_0 are the relaxation times for the phonon scattering by the impurities and by the pure metal, respectively. Since the electron-impurity interaction is elastic, we can write Eq. (5) in the form

$$\Delta S^e = \frac{S_0^e}{W_0^e T L_0/\Delta\rho+1}\left[\frac{\partial \ln\Delta\rho/\partial E}{\partial \ln\rho_0/\partial E}-1\right]_{E_F}. \tag{7}$$

Here L_0 is the Lorentz number ($L_0 = 2.45\times10^{-8}$ V^2/deg^2).

At high temperatures, S_0^g and ΔS^g become negligible because of the dominant influence of phonon scattering processes which do not involve electrons. Therefore, measurements at high temperatures can then be used directly to obtain S_0^e and ΔS^e. $\Delta S^e(T)$ can then be calculated for all temperatures using Eq. (5) or (7). The function $\Delta S^g(T)$ is then obtained from (4).

IV. EXPERIMENTAL RESULTS

The absolute thermopower S of pure annealed aluminum is shown in Fig. 1 as a function of temperature. Our data are in excellent agreement with those of Gripshover *et al.*,[22] who recently measured $S(T)$ for aluminum between 4.2 and 700°K. Points from the curve of Gripshover *et al.*, between 300 and 400°K, are indicated in Fig. 1. The change ΔS for the various alloys is given in Figs. 2–8 as a function of temperature. The values of $\Delta\rho$ and of ΔS(453°K) for the different specimens are listed in Table I. For the alloy Al+0.10 at.% Zn, two specimens were investigated which were made using alloy wire from the two different sources. It is seen from Fig. 5 and Table I that the material from the two different sources yielded the same results. The distribution of the gold admixture in the alloy Al+0.03 at.% Au is somewhat questionable because of the low solubility of Au in Al.[23] The small values of the impurity resistivity $\Delta\rho$ and of ΔS(453°K) for Al+0.03 at.% Au shown in Table I clearly suggests that the gold admixture is precipitated into clusters.

The dashed curves in Figs. 1–7 indicate the electronic components S^e and ΔS^e. They were obtained in the following way. Ricker and Schaumann[24] have measured the absolute thermopower of aluminum from 440°C beyond the melting temperature. Assuming that S_0^e is proportional to T, according to Eq. (2), and that S_0^g is negligible above about 450°C in aluminum, we extrapolated the data of Ricker and Schaumann at 450°C linearly to zero temperature to obtain the function $S_0^e(T)$. The fact that S_0^g is negligible above 450°C can be deduced from our result that in all aluminum alloys ΔS was independent of temperature above 350 to

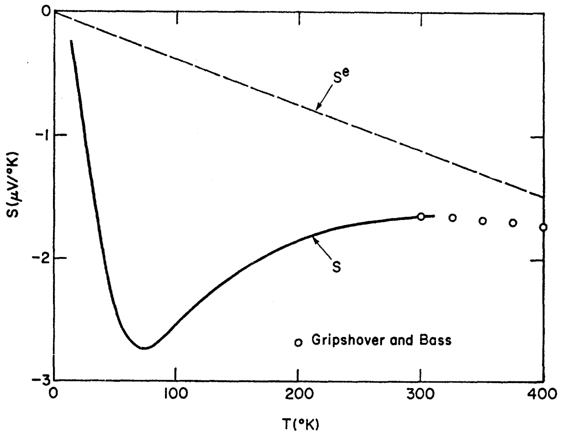

FIG. 1. Solid line: absolute thermopower of aluminum versus temperature. Dashed line: estimated electron diffusion component. The circles represent some data of Gripshover *et al.* (Ref. 22).

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[20] I. I. Hanna and E. H. Sondheimer, Proc. Roy. Soc. (London) **A239**, 247 (1957).

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[22] R. J. Gripshover, J. B. Vanzytveld, and J. Bass, Phys. Rev. **163**, 598 (1967).

[23] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Co., New York, 1958).

[24] T. Ricker and G. Schaumann, Physik Kondensierten Materie **5**, 31 (1966).

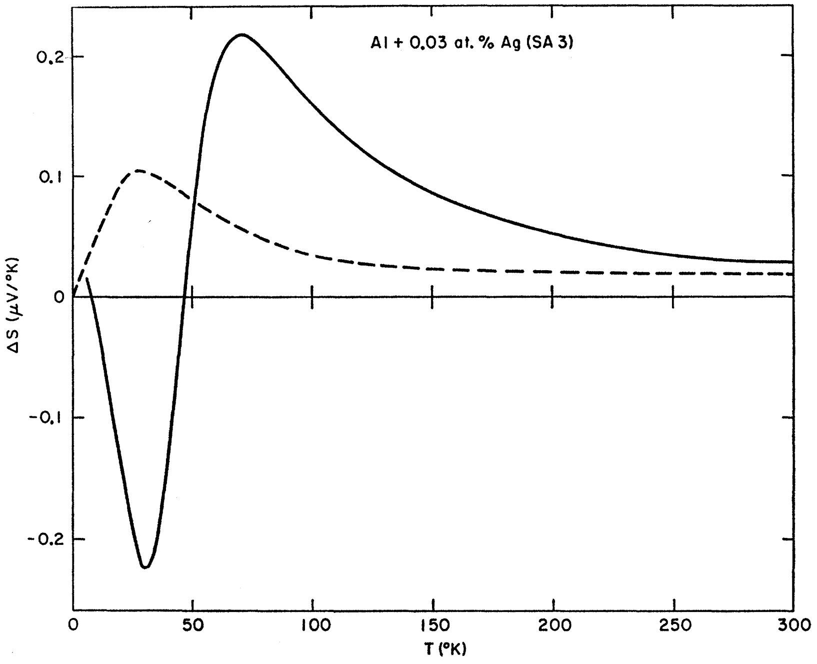

FIG. 2. Thermopower of the alloy Al+0.03 at.% Ag versus pure aluminum (solid line) and the difference ΔS^e in the electronic component (dashed line) as function of temperature.

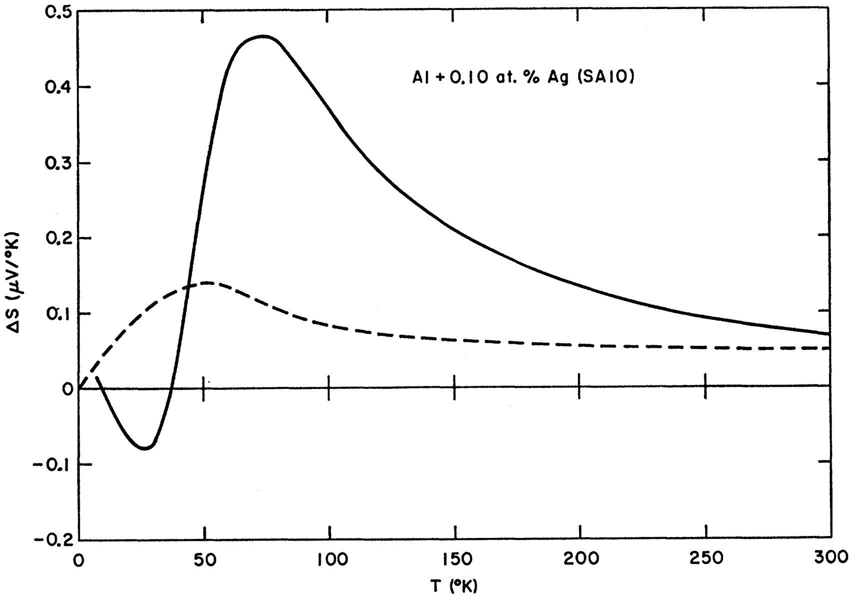

FIG. 3. Thermopower of the alloy Al+0.10 at.% Ag versus pure aluminum (solid line) and the difference ΔS^e in the electronic component (dashed line) as function of temperature.

400°K. From Eqs. (4)–(6) we see that at high temperatures a temperature-independent value of ΔS is only possible if ΔS^g is negligible. In this way we obtained

$$S_0^e/T = -3.7\times10^{-3}\ \mu V/°K^2, \qquad (8)$$

which is identical with the dashed straight line of Fig. 1. The temperature independence of ΔS above 350 to 400°K indicates that ΔS^g becomes negligible above this temperature range. We used the value $\Delta S(453°K) = \Delta S^e(453°K)$ to calculate the function $\Delta S^e(T)$ with Eq. (7). The thermal resistivity $W_0^e(T)$ was obtained from Fenton *et al.*[25] below 50°K. Above 50°K, $W_0^e(T)$ was found from the electrical resistivity $\rho_0(T)$,[26] assuming the Wiedemann-Franz law. In Figs. 2–7 the function $\Delta S^e(T)$, obtained in this way, is indicated by a dashed curve.

As seen from Fig. 1, the phonon-drag thermopower S_0^g in aluminum is negative with a peak of $|S_0^g| \approx 2.5$

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[25] E. W. Fenton, J. S. Rogers, and S. B. Woods, Can. J. Phys. 41, 2026 (1963).

[26] G. T. Meaden, *Electrical Resistance of Metals* (Heywood and Co. Ltd., London, 1965).

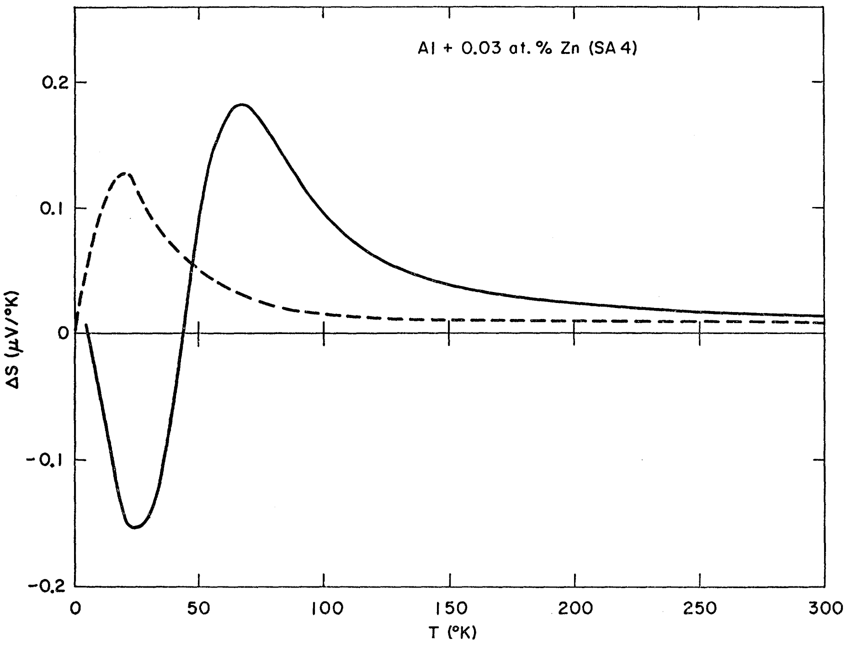

FIG. 4. Thermopower of the alloy Al+0.03 at.% Zn versus pure aluminum (solid line) and the difference ΔS^e in the electronic component (dashed line) as function of temperature.

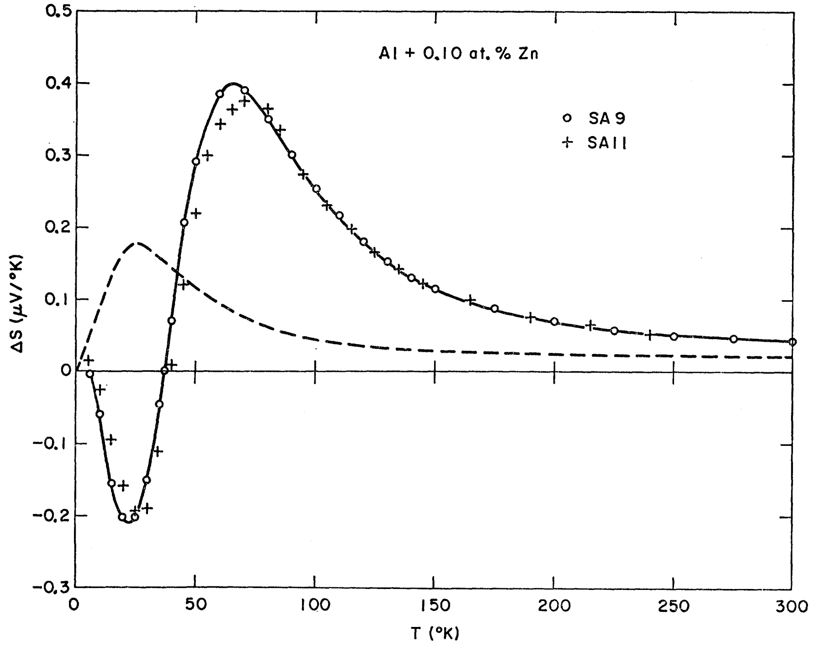

FIG. 5. Thermopower of the alloy Al+0.10 at.% Zn versus pure aluminum (solid line) and the difference ΔS^e in the electronic component (dashed line) as function of temperature. Circles: alloy from Sigmund Cohn, Inc.; crosses: alloy from Cominco American, Inc.

μV/°K at about 70°K. $S_0{}^g$ in aluminum stays negative down to 2°K, the lowest temperature investigated.[12] As seen from Figs. 2–7 the change ΔS^e in the alloys is positive. At higher temperatures, the solute ions cause a reduction in the phonon-drag component, as one would expect. Since magnesium and aluminum have about the same mass, the reduction of S^g at higher temperatures in the Al-Mg alloys is relatively small. Apparently, at low temperatures the solute ions cause an *increase* in $|S^g|$ for all alloys. The increase in $|S^g|$ at low temperatures, due to alloying, is also indicated in Fig. 8 for the alloy containing 0.03 at.% Au, where the separation into both components has not been carried out explicitly. The temperature where ΔS^g changes its sign lies between 40 and 50°K for the alloys containing silver and zinc, and between 70 and 80°K for the aluminum-magnesium alloys.

The separation of $S_0(T)$ of pure aluminum into the electron diffusion component and the phonon-drag component may be somewhat uncertain. The value given in Eq. (8) may be wrong by 10–20%. Gripshover *et al.*[22] have argued from their data on pure aluminum that the phonon-drag thermopower in aluminum may persist even up to the melting temperature. However, this appears rather unlikely in view of the fact that the change ΔS in the alloys is practically temperature-independent above 350 to 400°K.

V. DISCUSSION

We do not attempt to discuss the change ΔS^e or the reduction ΔS^g at higher temperatures quantitatively, but rather concentrate on the fact that $|S^g|$ increases at low temperatures because of alloying. The increased values of $|S^g|$ found in the dilute aluminum alloys at low temperatures remind us of similar anomalies observed in other systems.[5,8–11] As mentioned above, these anomalies have been explained by the anisotropy of the relaxation times for electron scattering.[5–7] Bailyn[6] has considered the anisotropic case in which different regions of the Fermi surface act differently. He showed that, after dividing the Fermi surface into different regions j, the total phonon-drag thermopower can be written in the form

$$S^g=\sum_j \frac{\sigma_j}{\sigma} S_j^g. \tag{9}$$

Here σ_j and S_j^g are the electrical conductivity and phonon-drag thermopower of region j, respectively; σ is the total conductivity. Equation (9) is particularly useful if the Fermi surface can be divided such that σ_j is approximately constant for each region. The advantage of Eq. (9) is then that it shows readily the influence of a change in the electron scattering (by introducing impurities) if the phonon scattering remains unchanged. At low temperatures, where only small phonon wave vectors are important, the electron-phonon transitions between different regions j can be neglected. Therefore, S_j^g is the phonon-drag thermopower one would obtain if region j would act alone. At higher temperatures the meaning of S_j^g is more general.[6] If σ_j involves impurity scattering, it includes, of course, at all temperatures a large number of transitions *between* regions.

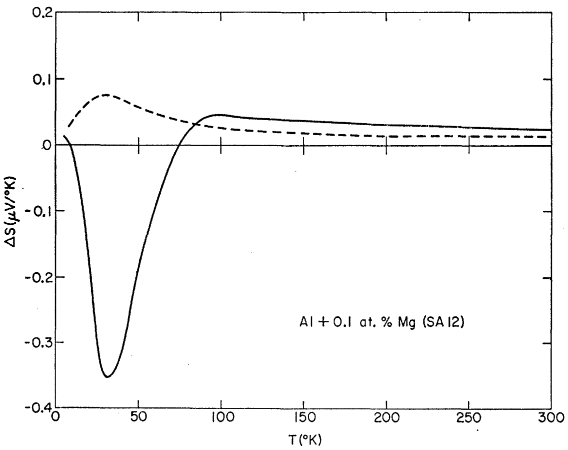

FIG. 6. Thermopower of the alloy Al+0.10 at.% Mg versus pure aluminum (solid line) and the difference ΔS^e in the electronic component (dashed line) as function of temperature.

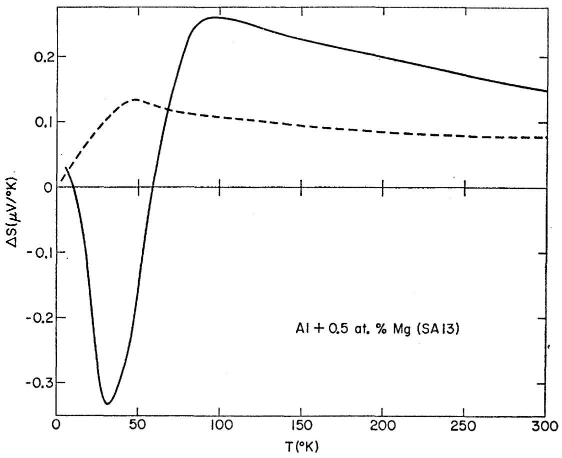

FIG. 7. Thermopower of the alloy Al+0.50 at.% Mg versus pure aluminum (solid line) and the difference ΔS^e in the electronic component (dashed line) as function of temperature.

Equation (9) has been derived earlier[27] within the two-band model. In the Peltier picture the derivation is as follows. We consider two conductors in parallel (Fig. 9) with the electrical conductivities σ_1 and σ_2, which carry the Peltier heat current Q_1 and Q_2. If U is the voltage drop across the circuit, the Peltier coeffi-

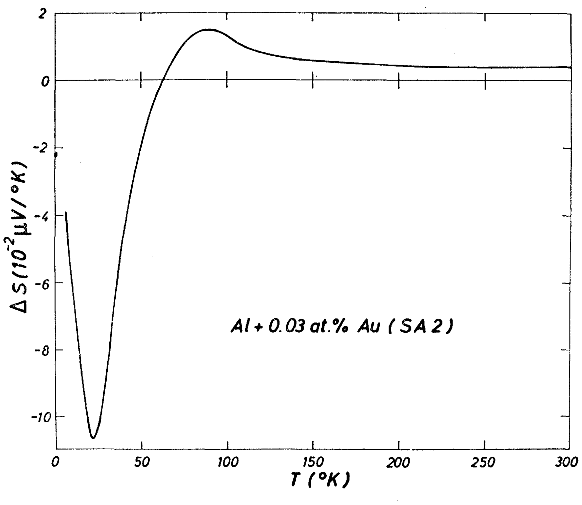

FIG. 8. Thermopower of the alloy Al+0.03 at.% Au versus pure aluminum as function of temperature.

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[27] A. H. Wilson, *The Theory of Metals*, (Cambridge University Press, New York, 1965), p. 205; D. K. C. MacDonald, *Thermoelectricity* (John Wiley & Sons, Inc., New York, 1962), p. 115.

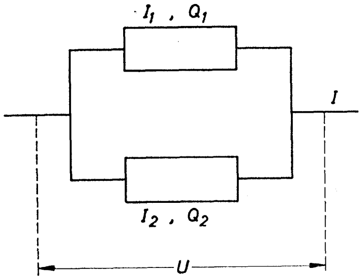

FIG. 9. Two parallel conduction bands.

cients for both conductors are given by

$$\pi_1=Q_1/U\sigma_1;\quad \pi_2=Q_2/U\sigma_2. \tag{10}$$

The Peltier coefficient of the circuit is

$$\pi=(Q_1+Q_2)/U\sigma=(\pi_1\sigma_1+\pi_2\sigma_2)/\sigma. \tag{11}$$

With the Thomson equation $\pi=ST$, we have the analog of Eq. (9). We note that this derivation is valid for both the electron diffusion component and the phonon-drag component.

We now turn to the low-temperature phonon-drag thermopower of the dilute aluminum alloys. Since at low temperatures the electron-phonon interaction causes only small angle electron scattering, the sign of S^g is determined by the local differential geometry of the Fermi surface. As has been emphasized by Ziman,[28] the sign of S^g at low temperatures is negative, if the phonon wave vector joining the two electron states crosses an *occupied* region of the Fermi surface (transition between points on an electron orbit). The sign of S^g is positive if the phonon wave vector crosses an *empty* region of the Fermi surface (transition between points on a hole orbit). The Fermi surface of aluminum is nearly a sphere, except near the edges where the sphere crosses a Brillouin-zone boundary.[29] Therefore, one would expect the low-temperature phonon-drag thermopower in aluminum to be negative, as found experimentally. We consider now the second band in aluminum. If the pseudopotential of the ions would be infinitely small, the edges of the second band would be quite sharp and the whole band would behave like free electrons. However, because of the finite pseudopotential of the ions, the edges of the second band are rounded off, resulting in narrow strips with hole character. For these strips S^g should be positive according to the Ziman criterium. Therefore, the contribution from the neighborhood of the edges of the second band tends to reduce the negative value of S^g resulting from the main portion of the second band.

For the third band in aluminum (monster), one would expect according to the Ziman criterium a negative contribution to the phonon-drag thermopower at low temperatures, where small-angle electron scattering prevails. However, because of the strong distortion of the parts of the Fermi surface, forming the third band, we expect here $|S^g|$ to be larger than for the main portion of the second band.

If we neglect the relatively small number of carriers in the fourth band, we can use the following crude arguments in combination with Eq. (9). We divide the Fermi surface of aluminum into three regions: (1) the area around the edges of the second zone (index 2*e*), (2) the third band (monster, index 3*m*), and (3) the rest (index *r*). Then we write

$$S^g=(\sigma_{2e}/\sigma)S_{2e}^g+(\sigma_{3m}/\sigma)S_{3m}^g+(\sigma_r/\sigma)S_r^g. \tag{12}$$

As indicated above, S_{3m}^g and S_r^g are negative, but $|S_{3m}^g|>|S_r^g|$. S_{2e}^g is positive. Now the essential point is that the weighting factors σ_{2e}/σ, σ_{3m}/σ, and σ_r/σ can be quite different, depending on whether the electrons are scattered predominantly by phonons or by impurities. To explain the effective enhancement of the negative phonon-drag thermopower in aluminum at low temperatures because of alloying, we have two possibilities. First, we can assume that

$$(\sigma_{2e}/\sigma)_{\mathrm{i}}<(\sigma_{2e}/\sigma)_{\mathrm{ph}} \tag{13a}$$

or

$$(\tau_{2e}/\tau)_{\mathrm{i}}<(\tau_{2e}/\tau)_{\mathrm{ph}}. \tag{13b}$$

Here, i and ph indicate electron scattering by impurities and by phonons, respectively. The τ's are the electron relaxation times. In this case the positive contribution S_{2e}^g would be reduced because of alloying. Second, we can assume

$$(\sigma_{3m}/\sigma)_{\mathrm{i}}>(\sigma_{3m}/\sigma)_{\mathrm{ph}} \tag{14a}$$

or

$$(\tau_{3m}/\tau)_{\mathrm{i}}>(\tau_{3m}/\tau)_{\mathrm{ph}}. \tag{14b}$$

In this case, the negative and rather large contribution S_{3m}^g would be enhanced because of alloying. The variation over the Fermi surface of the electron-impurity interaction, as a large-angle scattering event, is probably rather weak. Therefore, relations (13) and (14) suggest a strong variation of the electron-phonon interaction over the Fermi surface. Such a variation has been suggested recently by Brändli *et al.*[30] and by Holwech *et al.*[31] from measurements of the size effect on the electrical resistivity in aluminum and its temperature dependence. Whereas relation (13) would be difficult to understand, relation (14) appears to be more likely. Small-angle electron scattering is particularly effective in reducing the conductivity for the highly distorted parts of the Fermi surface in the third band. A similar result has been born out by Ziman[32]

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who showed for the noble metals that at low temperatures the relaxation time for electron-phonon scattering is appreciably shorter at the neck areas than at the belly areas.

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Helicon Waves, Surface-Mode Loss, and the Accurate Determination of the Hall Coefficients of Aluminum, Indium, Sodium, and Potassium*

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Observations of helicon wave resonances in some metals have been interpreted by various investigators as implying values for the Hall coefficients of these metals which are significantly higher than the theoretical values. This interpretation resulted from using an approximate solution to the relevant boundary-value problem, without a full appreciation of the extent of the errors which were thereby incurred. In 1964, Legéndy critically discussed the boundary conditions and gave several solutions. His solution for an infinite cylinder parallel to the static magnetic field is particularly interesting in that it predicts the existence of a surface mode whose total power dissipation is virtually independent of the resistivity of the material. This paper presents a detailed quantitative experimental confirmation of the accuracy of this solution, thus validating the boundary condition used. The observations also yield values for the Hall coefficients of aluminum, indium, sodium, and potassium which are equal to the theoretical values to within the experimental accuracy of about $\frac{1}{2}\%$.

I. INTRODUCTION

In 1962, Chambers and Jones[1] showed that the helicon-wave (magnetoplasma) resonance frequencies and line shapes which occur for a sample could be predicted from a knowledge of its Hall coefficient, resistivity, and shape, and from the geometry of the excitation and detection coil system. They suggested that the observation of helicon resonances could therefore be used to measure the Hall coefficients of a wide variety of materials, in particular, the simple metals at low temperatures. Since this method differs from the conventional one in permitting rather larger sample dimensions and in substituting a frequency measurement for voltage and current measurements, it would appear to be capable of substantially higher accuracy. They also pointed out that the theory of metals makes a clear prediction for the high-field limiting value of the Hall coefficient in metals with a closed Fermi surface. When they attempted to interpret their helicon-resonance observations on samples of lithium, sodium, potassium, aluminum, and indium in terms of the sample materials' Hall coefficients, however, they obtained values which were systematically about 5% high with an experimental uncertainty of only about 1%.

Since the resonance is evidence of a standing wave pattern in the sample, its frequency can be used to determine the sample material's Hall coefficient only if one has a sufficiently accurate solution to the helicon-wave–boundary-value problem relevant to the particular sample and coil geometry used. Chambers and Jones analyzed the case of a thin slab perpendicular to the static magnetic field, assuming no variation of the wave fields in the transverse directions (which could occur only in a plate whose transverse dimensions were infinite). Their principal conclusion was that resonance occurs when the sample thickness is an integral number of half-wavelengths. They calculated an approximate

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