Friedel Theory of Thermoelectric Power Applied to Dilute Magnesium Alloys

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A brief review is given of several theories of the thermoelectric power of alloys. The Friedel theory which states that the parameter $\Delta X = - (E_F - E_0)(\partial \log \Delta \rho / \partial E)$ is a constant is found to hold over a relatively wide range of compositions. The constant takes on values which depend upon the valence of the solute atom. A dependence upon the atomic number (or period) of the solute is also indicated.

INTRODUCTION

IN a recent paper,[1] (hereafter referred to as Paper I), we have reported on the measurement of a number of electron transport properties of dilute magnesium alloys. In the present paper we will concern ourselves primarily with the electrical resistivity and thermoelectric power at room temperature. Since it has become commonplace to state that little is known about the thermoelectric power of alloys, it seems germane to review some of the recent theoretical investigations.

Starting from the Boltzmann transport equation, Mott[2] derived the following expression for the absolute thermoelectric power at temperatures above the characteristic temperature θ.

$$S = -\frac{\pi^2 k^2 T}{3|e|}\left\{\frac{\partial \log \sigma(E)}{\partial E}\right\}_{E=E_F},$$

or

$$S = +\frac{\pi^2 k^2 T}{3|e|}\left\{\frac{\partial \log \rho(E)}{\partial E}\right\}_{E=E_F}, \quad (1)$$

where

$$\sigma(E) = \frac{2e^2}{\hbar^2}\int\left\{\frac{\partial E}{\partial k_x}\right\}^2 \tau(\mathbf{k})\frac{df}{|\text{grad}E|}, \quad (2)$$

and $\rho = \sigma^{-1}$. In the above, the integration is over the surface of constant energy E, e is the electronic charge, k and k_x are the wave number and its x component, and $\tau(\mathbf{k})$ is the relaxation time. The absolute thermoelectric power S, depends therefore upon the rate of change of σ (or ρ) with E; in turn, σ is determined by the mean free path and the effective mass of the electrons.

Soon afterwards, Muto[3] obtained for the thermoelectric power of the junction of a pure metal and a dilute solid solution of that metal, the expression

$$S = S_{\text{alloy}} - S_{\text{metal}}$$

$$= \frac{\pi^2}{3}\frac{k^2 T}{|e|}\left\{\frac{1}{dE/dk}\frac{\tau_T}{\tau_0 + \tau_T}\left(\frac{1}{\tau_0}\frac{d\tau_0}{dk} - \frac{1}{\tau_T}\frac{d\tau_T}{dk}\right)\right\}_{E=E_F}, \quad (3)$$

where τ_0 is the relaxation time due to the thermal vibrations of the atoms situated at the lattice sites, and τ_T is the relaxation time due to impurities.

With this analysis Muto was able to explain why the noble metals, on the one hand, are observed to have thermoelectric powers with positive signs, and the alkali metals, on the other, have thermoelectric powers with negative signs. Muto however did not attempt a quantitative comparison with the experimental data.

At the 1947 Bristol Conference, Crussard[4] reported measurements of the influence of dilute alloying elements on the thermoelectric power. Whereas it is known that the resistivity usually increases with alloying, Crussard showed this was not always the case for the thermoelectric power. As a result of this work Crussard stated a general law which he applied to aluminum alloys, namely, "if metal B is dissolved in small amounts in metal A, it will increase or decrease the thermoelectric power (of metal A), depending on whether B comes before or after A (in the groups of the periodic table with 8 columns). If A and B are in the same column, the effect is very small." He further suggested that this behavior could arise due to the local influence of a foreign atom on the electron density, creating electrically charged centers, positive or negative, depending on the respective number of valence electrons of both metals.

Galt[5] explained Crussard's aluminum data in terms of the variation of the band structure of aluminum due to alloying. Employing the assumption that the Fermi energy E_F depends upon the electron concentration of the alloy, and that the absolute value of the thermoelectric power S depends upon E_F, Galt concluded that a metal preceding aluminum should make it more negative, whereas a metal following aluminum should make it more positive. Thus, although the exact form of the variation of S with E_F could not be stated, the sign of the variation could, and it agreed with Crussard's observations.

More recently Friedel[6] has expressed the relative

[1] Salkovitz, Schindler, and Kammer, Phys. Rev. 105, 887 (1957).
[2] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Oxford University Press, New York, 1936); N. F. Mott, Proc. Roy. Soc. (London) A156, 368 (1936).
[3] T. Muto, Sci. Pop. Inst. Phys. Chem. Research 34, 741 (1937).
[4] C. Crussard, *Conference on Strength of Solids Report*, Bristol (Physical Society, London, 1948), p. 119.
[5] J. K. Galt, Phil. Mag. 40, 309 (1949).
[6] J. Friedel, J. phys. radium 14, 561 (1953).

TABLE 1. Compilation of data.[a]

Speci-men No.	Alloying agent	Atomic percent	Resistivity ρ_{20} (10^{-6} ohm cm)	Thermo-electric power $S300°K$	ΔX
1	Pure Mg		4.450	−0.223	
2	Ag	0.11	4.586	+0.015	−6.04
3		0.22	4.626	+0.148	−7.61
4		0.33	4.711	+0.268	−6.79
406		0.495	4.865	+0.575	−7.24
407		0.528	5.007	+0.795	−7.06
409		1.953	5.947	+1.79	−6.02
422	Li	0.49	4.875	+0.395	−5.18
156		2.55	6.377	+1.834	−4.94
117		4.42	7.668	+2.78	−5.26
396	Cd	0.55	4.883	+0.375	−4.88
397		1.01	5.141	+0.630	−4.51
398		1.92	5.734	+1.12	−4.21
725		8.64	9.664	+3.03	−4.24
400	Al	0.29	5.032	−0.102	0.25
401		0.53	5.583	−0.112	0.71
402		0.80	6.091	−0.143	0.93
403		1.64	7.688	−0.255	1.27
404		2.18	8.646	−0.397	1.52
405		2.41	9.064	−0.462	1.62
391	In	0.446	5.198	+0.039	−0.44
392		0.862	6.422	+0.062	0.36
393		1.46	7.617	+0.067	0.57
394		2.30	9.180	−0.057	0.91
395		3.01	10.287	−0.158	1.10
16		3.74	11.971	−0.421	1.48
13	Tl	1.32	8.772	+0.393	0.07
12		2.94	13.469	+0.647	0.03
380	Sn	0.047	4.786	−0.174	0.57
5		0.10	5.062	−0.370	2.30
381		0.17	5.452	−0.382	1.98
6		0.19	5.523	−0.499	2.48
7		0.29	6.001	−0.618	2.58
382		0.54	7.200	−0.909	2.82
383		1.08	9.606	−1.365	3.12
384		2.04	11.646	−1.625	3.25
65	Pb	0.24	5.782	−0.366	1.76
66		0.37	6.467	−0.502	2.01
388		1.32	11.276	−1.091	2.49

[a] The thermoelectric power data reported in this table were obtained relative to commercial purity magnesium wires. The thermoelectric power of specimen No. 1, pure magnesium, was also obtained relative to very high-purity copper wire from which the absolute value of $S300°K$ for pure magnesium was calculated to be $= -1.33 \mu v/C°$, and the parameter $X = 1.20$.

variation in thermoelectric power with alloying as

$$\frac{\Delta S}{S} = -\left(1 - \frac{\Delta X}{X}\right)\left(1 + \frac{\rho}{\Delta \rho}\right)^{-1}, \quad (4)$$

where

$$X = -(E_F - E_0)\frac{\partial \log\rho}{\partial(E_F - E_0)}, \quad (5)$$

$$\Delta X = -(E_F - E_0)\frac{\partial \log\Delta\rho}{\partial(E_F - E_0)}.$$

E_F is the Fermi limit and E_0 is the energy at the

bottom of the conduction band. The bases for this relation were the use of the one-electron approximation, the condition that the temperature was greater than the Debye temperature, the validity of Eq. (1), and the assumption that E_F remains constant as long as the concentration is low, e.g., the impurities do not interact [Friedel[7]].

Also starting from Eq. (1), Domenicali and Otter[8] presented a semiempirical theory which relates the absolute thermoelectric power to the dependence on energy of the scattering cross section $Q(E)$ of a lattice imperfection or impurity. Numerical values are deduced for the first few scattering coefficients in a Taylor's expansion of $Q(E)$ about the Fermi level of the pure solvent. In this analysis, it is assumed that as alloying takes place the Fermi level is displaced. Because of complexities inherent in treating a divalent metal and its alloys in this fashion, we have not used the Domenicali theory in our analysis.

APPLICATION OF THE FRIEDEL THEORY

The form of the Friedel theory is such that it is quite simple to investigate its applicability to dilute magnesium alloys, particularly with the data available in Paper I. To obtain the absolute value of the thermoelectric power of magnesium, the thermoelectric power was measured relative to a piece of high-purity copper wire which had in turn been compared with a standard platinum sample. The resulting value for pure magnesium was found to be $-1.33 \mu v/°C$. The parameter X can be calculated directly from Eq. (1) by using the Fermi level of 6.4 ev as obtained by Trlifaj.[9] Knowing ρ, and the changes $\Delta\rho$ and ΔS in the resistivity and thermoelectric power due to alloying, it is therefore possible to calculate ΔX for the series. The results are tabulated in Table I, and are plotted in Fig. 1.

Three striking features of the data are evident in the graph:

First, for a given alloying element the parameter ΔX tends to be constant. The extent to which ΔX is constant is surprising, and implies that there is little interaction between the impurity atoms even up to the neighborhood of the solubility limits of these alloy systems. (The scatter of the data for the whole magnesium-silver alloy series and at the very low concentrations in the magnesium-tin alloys is probably a reflection of experimental errors.)

Secondly, it is to be noted that the data fall into groups of curves. The curves representing the monovalent additions silver and lithium lie below the curve representing the data obtained from divalent cadmium additions. Similarly the curves representing the trivalent additions aluminum, indium, and thallium are all above the magnesium-cadmium curve, and the

[7] J. Friedel, Phil. Mag. 43, 153 (1952).
[8] C. A. Domenicali and F. A. Otter, Phys. Rev. 95, 1134 (1954).
[9] M. Trlifaj, Czechoslov. J. Phys. 1, 110 (1952).

curves representing the quadrivalent addition tin and lead are above these. In addition, the monovalent and divalent solutes produce a negative ΔX, whereas the trivalent and quadrivalent solutes produce a positive ΔX.

Finally in each equal-valent group, the alloying addition with the largest atomic number (or weight) gives the smallest value of ΔX.

Friedel[10] has compiled values of ΔX for impurities in copper, silver and gold, and finds ΔX to be positive and of the order unity. This means that in alloys of noble metals $\Delta \rho$, the change in resistivity due to alloying, decreases slowly with increasing energy. When ΔX is negative, then $\Delta \rho$ must increase with increasing energy. In the case of the magnesium alloys we find that when ΔZ is greater than zero, ΔX is also greater than zero, and vice versa. Here ΔZ is the difference in valence between solute and solvent. It is thus evident that for the trivalent and quadrivalent additions to magnesium, $\Delta \rho$ decreases with increasing energy; for the divalent and monovalent additions, $\Delta \rho$ increases with increasing energy.

DISCUSSION

In Paper I we demonstrated that the thermoelectric power for a given dilute magnesium alloy could be expressed as the sum of two contributions. One contribution, S_e, arises from the direct effect of electron concentration and is linear with concentration; the other, S_i, arises from all other effects, notably the perturbation upon the ion-core potential.

It is desirable, at this point to determine whether the Friedel model conflicts with the above. To do this, let us assume that we have a sample of pure magnesium. Its thermoelectric power is given by Eq. (1):

$$S_{\mathrm{Mg}} = \frac{\pi^2 k^2 T}{3|e|}\left(\frac{\partial \log \rho}{\partial E}\right). \qquad (6)$$

If we add a solute, we may change the electronic concentration, which in turn will have an effect upon the thermoelectric power. We may also produce a perturbation on the ion-core potential due to lattice strains, which will contribute to the thermoelectric power. The latter effect S_i may be studied by adding cadmium to magnesium, because cadmium is divalent and therefore the electron concentration is not changed. If instead we add a trivalent solute, such as indium, the electronic concentration of the alloy does change. That portion of the thermoelectric power of the magnesium-indium alloys due to the *total* electron concentration may then be expressed as

$$S_e' = \frac{\pi^2 k^2 T}{3|e|}\left\{\frac{\partial \log(\rho + \Delta \rho_e)}{\partial E}\right\}_{E=E_F}, \qquad (7)$$

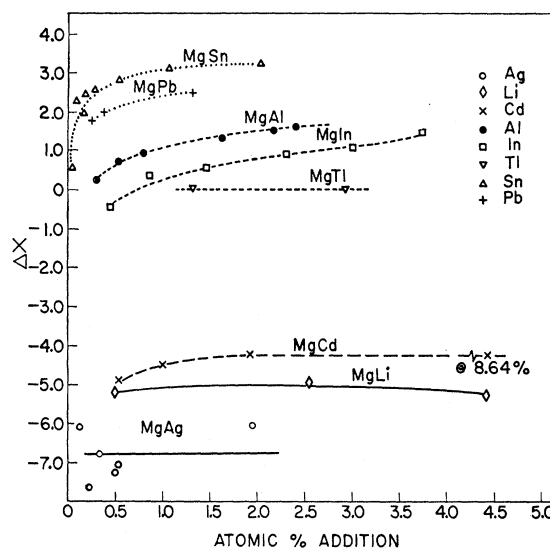[10] J. Friedel, Can. J. Phys. 34, 1190 (1956).

FIG. 1. Plot of ΔX *versus* composition for dilute magnesium alloys.

where $\Delta \rho_e$ is the change in resistivity due to the change in the number of conduction electrons. The portion of the thermoelectric power due only to the change in electron concentration, which we label S_e, is given by

$$S_e = S_e' - S_{\mathrm{Mg}}, \qquad (8)$$

$$S_e = -S_{\mathrm{Mg}}\left(\frac{\Delta \rho_e}{\rho + \Delta \rho_e}\right) + \frac{\pi^2 k^2 T}{3|e|}\left(\frac{1}{\rho + \Delta \rho_e}\right)\frac{\partial \Delta \rho}{\partial E}. \qquad (9)$$

It may be noted that in Paper I, we have taken

$$S_e = S_{\mathrm{alloy}} - S_{\mathrm{Cd}}, \qquad (10)$$

where S_{alloy} is the measured thermoelectric power of a magnesium alloy of given solute concentration, S_{Cd} is the thermoelectric power of a magnesium-cadmium alloy of the same cadmium concentration. It is quite evident that S_e in Eqs. (9) and (10) are identical. In Fig. 2 (identical with Fig. 14 in Paper I) are plotted the values of S_e obtained for the various alloys by use of Eq. (10). It is seen that S_e is proportional to the electron concentration and that the proportionality constant depends on ΔZ. Indeed if ΔZ is positive, S_e is negative. Since S_{Mg} is negative, then $\partial \Delta \rho / \partial E$ is negative or $\Delta \rho$ decreases with increasing energy as the above investigation of ΔX had indicated. If ΔZ is negative, then S_e is positive. For this case, however, we can only say that $\Delta \rho$ may increase or decrease with energy, although a limit exists on the extent to which $\partial \Delta \rho / \partial E$ may be negative.

It appears evident then that the application of Friedel's theory in no way negates the analysis given in Paper I.

As stated above, for alloys of the noble metals Friedel has shown that ΔX has values in the neighborhood of unity. It is pertinent, therefore, to inquire why
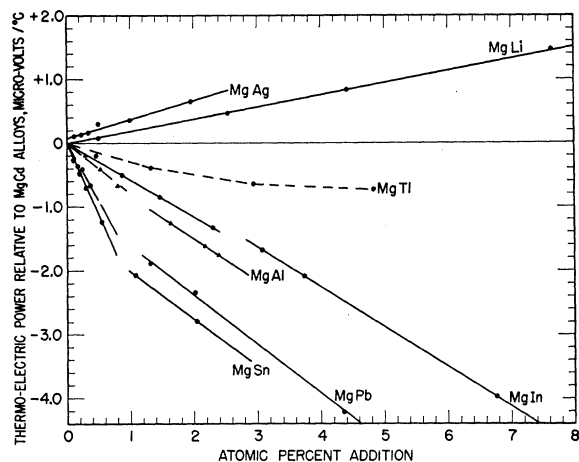
FIG. 2. Thermoelectric power relative to that of magnesium-cadmium alloys (S_e) versus composition. The breaks in the curves for MgIn, MgAl, MgPb, and MgSn are discussed in terms of Brillouin zone overlap in Paper I.

the various values for ΔX depending upon ΔZ, appear for the magnesium alloy system. In calculating the resistivity increment due to alloying, de Faget and Friedel[11] assume a one-electron model, and use the partial-wave method to derive the effective scattering cross section of the impurity atoms. The latter quantity is given in terms of the phase shifts η_l arising in the scattering of an electron by a perturbing potential, V_P. For this model it follows that

$$\Delta\rho = \frac{4\pi C}{N\Omega k_M} \sum l \sin^2(\eta_{l-1} - \eta_l). \qquad (11)$$

Here, C is the concentration of impurities, Ω is the atomic volume, and k_M is the momentum of the conduction electrons at the Fermi limit.

The value of the perturbing potential V_P is given by applying the Friedel sum rule[7] which states that this potential displaces in the Fermi gas a screening charge just equal to the excess (or deficient) nuclear charge ΔZ of the impurity. The charge displaced in the lth spherical harmonic is equal to $(2/\pi)(2l+1)\eta_l(k_M)$, so that

$$\Delta Z = (2/\pi)\sum_l(2l+1)\eta_l(k_M). \qquad (12)$$

[11] P. de Faget de Casteljau and J. Friedel, J. phys. radium 17, 27 (1956).

Providing the assumed perturbing potential extends over the radius of the atomic sphere and obeys the above sum rule, the form of the potential does not seem to be important, at least for the copper alloys. Probably for this reason ΔX does not change with ΔZ in these alloys. Friedel[12] has informed us that in the case of aluminum alloys ΔX varies with ΔZ as well as in the magnesium alloys. Retaining the free-electron model, he suggests the variation in ΔX can be explained by considering a potential which is repulsive for $\Delta Z < 0$ and attractive for $\Delta Z > 0$. Even strongly attractive potentials give phase shifts η_l which decrease with increasing energy at the Fermi level. On the other hand, repulsive potentials strong enough to repel locally a charge $|\Delta Z| \geq 1$ would give negative phase shifts which increase in absolute magnitude at the Fermi level (see Mott and Massey[13]) and would provide the proper dependence upon the sign of ΔZ.

In addition, Blatt[14] has suggested that for the magnesium alloys the value of ΔX may depend upon the shape of the well, which is influenced by the nature of the impurity.

CONCLUSIONS

It has been demonstrated that the Friedel theory of the thermoelectric power of alloys may be applied to dilute binary solid solutions of magnesium. The parameter $\Delta X = -(E_F - E_0)(\partial \log\Delta\rho/\partial E)$ has been shown to be constant for a given alloy up to the neighborhood of the solubility limit of the alloy in question. The value of ΔX is significantly dependent upon ΔZ, the difference in valence between solute and solvent atoms. Finally there is a slight dependence, for a given value of ΔZ, upon the atomic number of the impurity atom, that is, upon the row in the periodic table to which the solute belongs.

[12] J. Friedel (private communication).
[13] N. F. Mott and H. S. W. Massey, The Theory of Atomic Collision (Clarendon Press, Oxford, 1949), p. 32.
[14] F. J. Blatt (private communication).