R. E. Jones, Jr.

A Thermodynamic Treatment of Dilute Superconducting Alloys

Abstract: The effect of adding small concentrations of an impurity to a superconducting metal is analyzed by thermodynamic methods. Two possible types of variation of the Gibbs free energy with composition are then discussed, utilizing a number of simplifying assumptions. For the case in which alloys have a superconducting second-order transition, there is a long-range interaction among solute atoms, even in limits of high dilution.

Introduction

For many years the methods of thermodynamics have been successfully used to describe the transition between the normal and superconducting states.[1] Recently, a number of measurements have been made of the superconducting properties of alloys containing controlled amounts of impurities.[2-4] This paper is concerned with developing a thermodynamic treatment of the variation of free energy in a dilute superconducting alloy using composition as a parameter and, in particular, discusses two possible dependences of the free energy on composition.

One possibility is the assumption of a linear variation of the free energy with composition, which is equivalent to assuming that each atom added has an effect independent of those previously added. This hypothesis results in the prediction of a *first-order transition* in the absence of field for dilute alloys and an *infinite slope of critical field* at the critical temperature. The conventional thermodynamic treatment assumes a second-order transition and a finite slope.

A second approach is to assume that a second-order transition and a finite initial slope of the critical field at the transition temperature are established properties of dilute superconducting alloys. In this case it is shown that there is a cooperative interaction due to solute atoms even in the range of very high dilution.

General thermodynamic relations

In discussing the effect of diluting an initially pure superconductor, we will assume that specification of the temperature T, external magnetic field H, and the atom percent solute (the element present in smallest amount) x, describes the state of a specimen. The "Gibbs free energy per mole" g, of a system with these parameters is

$$g(H,T,x)=u-sT-mH,$$

where u is the internal energy per mole, s is the entropy per mole, and m is the magnetization per mole. From thermodynamics it follows that

$$dg=-sdT-mdH+\mu dx. \qquad (1)$$

The function μ is called the chemical potential and is defined as being equal to $(\delta g/\delta x)_{T,H}$.

Consider now the transition from the superconducting to the normal state, i.e., the *$s\leftrightarrow n$ transition*. The criterion that the two phases be in equilibrium at a given magnetic field, temperature, and composition is that the free energies of the two phases be equal. Therefore, if expressions may be found for the free energies in the normal and superconducting states, the equation

$$g_n(T,H,x)=g_s(T,H,x)$$

fixes the surface on which the phases are in equilibrium in T, H, x space. For increments of temperature, field, and composition which result in moving from one point on the $s\leftrightarrow n$ surface to another, we obtain from Eq. 1:

$$\begin{aligned} dg_n&=-s_ndT_c-m_ndH_c+\mu_ndx \\ &=dg_s=-s_sdT_c-m_sdH_c+\mu_sdx. \end{aligned}$$

This equation implies:

$$\frac{s_n-s_s}{m_n-m_s}=-\left(\frac{\delta H_c}{\delta T}\right)_x, \qquad (2)$$

$$\frac{\mu_n-\mu_s}{s_n-s_s}=\left(\frac{\delta T_c}{\delta x}\right)_H, \tag{3}$$

$$\frac{\mu_n-\mu_s}{m_n-m_s}=\left(\frac{\delta H_c}{\delta x}\right)_T, \tag{4}$$

and

$$\left(\frac{\delta H_c}{\delta x}\right)_T=-\left(\frac{\delta H_c}{\delta T}\right)_x\left(\frac{\delta T_c}{\delta x}\right)_H. \tag{5}$$

Here H_c is the field at which the $s\leftrightarrow n$ transition occurs for a given composition and temperature. Similarly, T_c is the temperature at which the $s\leftrightarrow n$ transition occurs at a given composition and field. (This is not the usual definition of T_c, nor is it the definition that we shall use in the remainder of the paper.)

If it is assumed that the magnetic moment and susceptibility of the normal metal is negligible for all magnetic fields, temperatures, and compositions, and if in addition we assume the superconducting phase is always perfectly diamagnetic, then

$$m_s=-\frac{v}{4\pi}H,$$

and from Eqs. 2 and 4,

$$s_n-s_s=-\frac{v}{4\pi}H_c\left(\frac{\delta H_c}{\delta T}\right)_x, \tag{6}$$

and

$$\mu_n-\mu_s=\frac{v}{4\pi}H_c\left(\frac{\delta H_c}{\delta x}\right)_T. \tag{7}$$

If it is found that when the critical magnetic field is plotted against temperature the slope at zero field, $(\delta H_c/\delta T)_{x,\,H_c=0}$, is finite, then these equations imply that the $s\leftrightarrow n$ transition is second-order in the absence of field. Thus

$$s_n-s_s=-\frac{H_c}{4\pi}\left(\frac{\delta H_c}{\delta T}\right)_x=0, \qquad \text{at } H_c=0. \tag{8}$$

Similarly, observing that the initial slope $(\delta H_c/\delta x)_{T,\,H_c=0}$, is finite implies

$$\mu_n-\mu_s=-\frac{H_c}{4\pi}\left(\frac{\delta H_c}{\delta x}\right)_T=0, \qquad \text{at } H_c=0. \tag{9}$$

It can be shown that if the slope of the critical temperature with composition $(\delta T_c/\delta x)_{H_c=0}$, is finite, then a second-order transition implies Eq. 9, and conversely Eq. 9 implies a second-order transition. To prove this statement it is sufficient to show that the difference in chemical potential is zero if, and only if, the difference in entropy is zero, and to show that the slope of the critical field with temperature is finite if, and only if, the slope of critical field with composition is finite. Equation 3 shows the former relation, and Eq. 5, the latter.

The dilute-solution approximation

One possible assumption regarding the variation of the Gibbs potential with composition is that the difference varies linearly with composition at a fixed temperature. Since this hypothesis is equivalent to the "dilute-solution approximation" which has been widely used in thermodynamics literature (see Reference 5, for example), we shall introduce the assumptions in the customary manner in the form of the equations

$$\mu_n=w_n(T)+RT[\ln x-\ln(1-x)] \tag{10}$$

and

$$\mu_s=w_s(T)+RT[\ln x-\ln(1-x)], \tag{11}$$

where the functions $w_n(T)$ and $w_s(T)$ are unspecified except in that they depend only on the temperature. The fact that the chemical potentials do not depend on field follows from the assumptions made about the magnetic behavior of the normal and superconducting phases. The form of these equations follows from the assumption that each solute atom substituted into the system has the same effect as the atoms previously substituted, except for a change in the entropy of mixing reflected in the second term. An example of the meaning of such equations would be where the only effect of dilution was the addition or depletion of "free" electrons in the metal, in which case the functions $w(T)$ would be proportional to the Fermi energies of the electrons of the normal and superconducting states.

Subtracting Eq. 11 from Eq. 10 and using Eq. 7, we see that the entropy of mixing terms cancel, and thus

$$\mu_n-\mu_s=w_n(T)-w_s(T)=\frac{v}{4\pi}H_c\left(\frac{\delta H_c}{\delta x}\right)_T. \tag{12}$$

Integration of this equation yields

$$\begin{aligned}(\mu_n-\mu_s)x&=\{w_n(T)-w_s(T)\}x\\&=\frac{v}{8\pi}\{H_c^2(x,T)-H_c^2(0,T)\}.\end{aligned} \tag{13}$$

From the latter equation it can be seen that if at a given temperature there is a composition at which the critical field of the dilute solution is zero (i.e., $H_c(x',T)=0$) while the pure material is superconducting (i.e., $H_c(0,T)>0$), then the chemical potential of the superconducting metal is less than that of the normal metal at that temperature. Experimentally this is frequently found to be the case.[2-4] If at that same temperature the slope of the critical temperature with composition is finite and nonzero, then by Eq. 3 we see that even in the absence of applied field the difference in entropy between the two phases is nonzero at the transition. In other words, instead of a second-order transition in the absence of field the transition is first order.[6]

The occurrence of a first-order transition in the absence of field could, of course, be detected by observing a latent heat in the transition. Moreover, certain other limiting features of the behavior of the critical field and critical temperature would also be observable. From Eq. 7 we see that, at a fixed temperature, the slope of the critical field versus composition would be negative and infinite at the point where the critical field was zero. Similarly, by Eq. 6, the slope of the critical field with temperature would be infinite at the same point. If upon sufficient dilution, the critical temperature is depressed to absolute zero (i.e., $T_c(x)=0$), then since the Nernst heat theorem states that the entropy difference between the two phases must vanish at absolute zero, we see from Eq. 3 that the slope of the critical temperature must be negative and infinite at that limit.

From these considerations we see that the dilute-solution approximation, when applied to dilute, nonmagnetic superconductors, predicts at least two features which are not usually considered to be characteristic of superconductors. These features are a first-order transition in the absence of field and an infinite initial slope of the critical field with temperature. It should be added that at least for alloys which have T_c depressed only a small amount below the T_c of the pure material, rather careful experiments would be required to see these two effects. Figure 1 shows the predicted variation of critical field with composition for indium alloys near the transition temperature of pure indium. As can be seen, the curvature leading to the infinite slope of critical field occurs largely below 1 gauss, which is in the order of the earth's magnetic field. The latent heat which is calculated for transitions in alloys in the absence of field is also small and would require rather careful experiments to detect.

Alloys with second-order transitions

Since there are no experiments which show these two features and, in fact, the available data seems to indicate that the transition is actually second order. The work of Doidge[7] with tin-indium alloys, for example, shows a linear slope of critical field with temperature at critical fields of approximately 0.25 gauss. It is only natural to question whether the dilute-solution approximation can be applied to the phenomena of superconductivity. It is perhaps better to turn to the problems of constructing a form for the chemical potential which will predict a second-order transition in the absence of field.

We shall find it convenient to rephrase our criteria slightly for a second-order transition in terms of the free-energy difference in the absence of field. If at a fixed temperature there exists a composition x' at which the critical field is zero (i.e., $H_c(x',T)=0$) while the pure material is superconducting (i.e., $H_c(0,T)>0$), we require for the two phases to be in equilibrium at the point x':

$$g_n(x', T) - g_s(x', T) = 0.$$

Furthermore, from the definition of the chemical potential and the necessary requirements for a second-order transition, the following equation must also hold at any composition and temperature at which there is a second-order transition:

$$\mu_n - \mu_s = \frac{\delta}{\delta x}[g_n - g_s] = 0.$$

It can be seen that the simplest polynomial expression for the difference in free energy that will predict a second-order transition is

$$g_n - g_s = C(T)[x'(T) - x]^2 = \frac{v}{8\pi} H_c^2, \tag{14}$$

where $x'(T)$ is the composition at which the normal and

Figure 1 **Dependence of critical field on composition.** *The experimental data are the critical field of pure indium and the transition temperature of an* In-Hg *alloy containing 0.505 at. %* Hg. *The intercept points are preliminary data from Reference 4.*

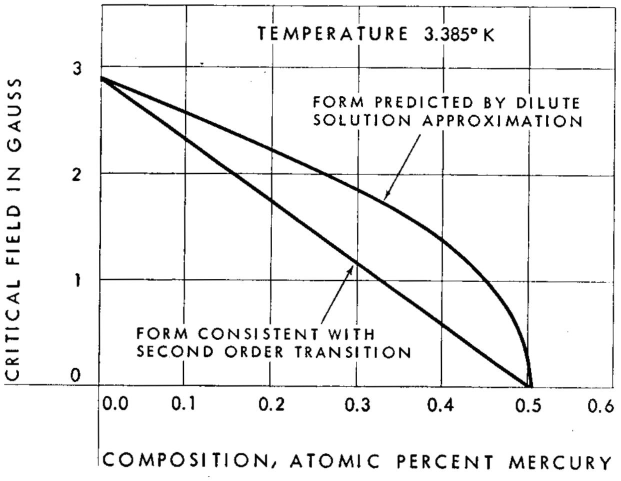
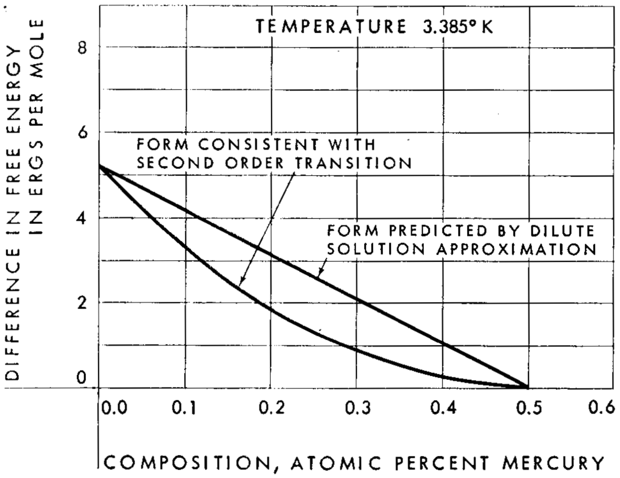


Figure 2 **Dependence of the difference in Gibbs free energy on composition.** *The experimental data are for pure indium and the transition temperature of an* In-Hg *alloy containing 0.505 at. %* Hg. *The intercept points are preliminary data from Reference 4.*



superconducting phases are at equilibrium in the absence of field, and $C(T)$ is a function of temperature which may be determined by requiring that Eq. 14 give correctly the free energy of the pure material. It can be seen from Eq. 14 that the requirement for a second-order transition in the absence of field leads to the conclusion that, in contrast to the dilute-solution approximation, the critical field, rather than the Gibbs free energy, is linear with composition. This, in fact, has been an implicit assumption made in constructing limiting laws obeyed by dilute, superconducting alloys. In the Appendix an expression with the form of Eq. 14 is developed using a number of these limiting laws.

Differentiation of Eq. 14 with respect to the percentage of solute yields an expression for the difference in chemical potential:

$$\mu_n - \mu_s = 2C(T)x'(T) - 2C(T)x. \tag{15}$$

When this expression is compared with Eq. 12 it can be seen that the difference in chemical potential in this case has a linear relationship to the percentage of solute. It should be pointed out that this is not simply a linear "correction," but rather that the magnitude of the two terms on the right of the equation must become equal at the critical temperature, i.e., at $x = x'(T)$, regardless of the magnitude of $x'(T)$. Just as an equation for the difference of chemical potential which is independent of composition (such as Eq. 12) indicates that each solute atom substituted has an effect independent of those previously substituted, an expression such as Eq. 15 points out the essential cooperative nature of dilution.

Conclusion

In Figures 1 and 2 the variations of critical field and difference in free energy are compared for the two cases. The dilute-solution assumption, in addition to predicting an infinite initial field with composition, implies a first-order transition in the absence of field and an infinite initial slope of critical field with temperature. On the other hand, the second compositional variation was deduced by requiring that the transition be second order and the initial slope of critical field with temperature be finite.

The experiments which have been reported in the literature show no examples of either of the two features implied by the dilute-solution approximation, although only a limited number of superconductors and solutes have been carefully studied. The situation might be that the linear variation of free energy holds true for some solutes, e.g., solutes having a magnetic spin, as suggested by Suhl and Matthias.[8] The other variation would then hold for other solutes, e.g., Group B elements dissolved in Group B superconductors. In the last analysis the choice between these two cases must be made for individual superconductors and solutes by precise measurements near the critical temperature.

Appendix

It should be pointed out that Eq. 13 is of a form convenient for calculating the entropy and heat capacity as explicit functions of composition. We shall obtain these expressions for small impurity contents using several limiting laws which have been suggested as representing the behavior of dilute alloys. We assume the "similarity principle," that is, that all the alloys obey the same equations for the reduced critical field, $H_c(T,x)/H_c(0,x)$, in terms of the reduced temperature, $T/T_c(x)$. Using the parabolic dependence of critical field on temperature for simplicity:

$$H_c(T,x) = H_c(0,x)\left[1 - \left(\frac{T}{T_c(x)}\right)\right]^2,$$

and the "law of corresponding states"[9]:

$$H_c(0,x) = \alpha T_c(x),$$

where α is independent of composition, we can obtain on differentiation with respect to composition:

$$\frac{\delta H_c}{\delta x}(T,x) = \alpha \frac{\delta T_c}{\delta x}(x)\left[1 + \left(\frac{T}{T_c(x)}\right)^2\right].$$

Since we are interested in alloys with small amounts of impurities, we use a result of Chanin, Lynton and Serin,[2] who found that for small compositions the slope of critical temperature versus composition is linear (i.e., $\delta T_c/\delta x = D$, a constant). In the last factor on the right we can substitute for $T_c(x)$ the critical temperature of the pure material. Our expression now is a function of temperature only and contains only constants characteristic of the pure material and the slope of critical temperature with composition, i.e.,

$$\frac{\delta H_c}{\delta x}(T) = \alpha D\left[1 + \left(\frac{T}{T_c(0)}\right)^2\right].$$

Integration yields an expression of the form of Eq. 14:

$$g_n - g_s = \frac{v}{8\pi}\left[H_c(T,0) + x\frac{\delta H_c}{\delta x}(T)\right]^2.$$

Differentiation by temperature gives the difference in entropy:

$$s_n - s_s = \frac{v}{4\pi}\left[H_c(T,0) + x\frac{\delta H_c}{\delta x}(T)\right] \times \left[\frac{\delta H_c}{\delta T}(T,0) + x\frac{\delta}{\delta T}\frac{\delta H_c}{\delta x}(T)\right].$$

Similarly for the difference in heat capacity:

$$c_n - c_s = \frac{Tv}{4\pi}\left[\frac{\delta H_c}{\delta T}(T,0) + x\frac{\delta}{\delta T}\frac{\delta H_c}{\delta x}(T)\right]^2 + \frac{Tv}{4\pi}\left[H_c(T,0) + x\frac{\delta H_c}{\delta x}(T)\right] \times \left\{\frac{\delta^2}{\delta T^2}H_c(T,0) + x\frac{\delta^2}{\delta T^2}\left[\frac{\delta H_c(T)}{dx}\right]\right\}.$$

Acknowledgments

The author wishes to thank Drs. Ittner, Seraphim and Senko of the IBM Research Laboratory for their many helpful discussions of this work. He is also indebted to M. D. Reeber of this laboratory for obtaining the results on superconducting indium-mercury alloys before publication.

References

1. See, for example, D. Schoenberg, *Superconductivity,* Cambridge University Press, 1952, Chapter III.
2. G. Chanin, E. A. Lynton, and B. Serin, *Phys. Rev.* **114,** 719 (1959).
3. E. A. Lynton, B. Serin and M. Zucker, *J. Phys. Chem. Solids,* **3,** 165 (1957).
4. M. D. Reeber, "Superconductivity of Indium-Mercury Alloys" (Submitted to the *Physical Review*).
5. R. Fowler and E. A. Guggenheim, *Statistical Thermodynamics,* Cambridge University Press, 1952, Chapter VIII.
6. This result was pointed out by Suhl and Matthias as a consequence of an equation analogous to Eq. 12 which resulted from a quantum-mechanical perturbation calculation of the effect of magnetic impurities on the electronic wave function in the normal and superconducting states. We see here, however, that the absence of a second-order transition is a consequence of any linear variation of the difference in free energy regardless of its cause. See H. Suhl and B. T. Matthias, *Phys. Rev.,* **114,** 977 (1959).
7. P. R. Doidge, *Proc. Roy. Soc.,* **248A,** 553 (1955).
8. Suhl and Matthias, *op. cit.,* p. 986.
9. Serin states that this assumption is valid for impurity concentrations less than a few tenths of one percent. See B. Serin, *Progress in Low Temperature Physics,* Vol. 1, Interscience Publisher Inc., New York, 1958, p. 148.

Received April 20, 1959