

Resistivity and Thermoelectric Power of Transition Metals in Copper-Gold Alloys

M. D. BLUE

Honeywell Research Center, Hopkins, Minnesota

(Received April 7, 1961)

Resistivity and thermoelectric power measurements on CuAu alloys containing dilute amounts of Co, Fe, and Mn are discussed. An analysis of these measurements using the thermoelectric power formula of Mott leads to values of the scattering cross sections of transition elements and their derivatives with respect to energy in good agreement with the values obtained for these elements with Cu or Au as solvent. The results indicate that contributions to resistance due to disorder scattering and impurity scattering are additive in these alloys.

INTRODUCTION

IN a previous paper,¹ the effects (resistivity and thermoelectric power) of dilute amounts of Ni in a CuAu host lattice were interpreted in a conventional manner using the thermoelectric power of Mott and Jones.² For this specific alloy system, the effect of Ni on the electrical properties of CuAu led to values for a scattering parameter and its energy derivative similar to values obtained from a study of the effects of Ni in pure Cu.

Through such measurements, information may be obtained concerning features of the electronic behavior of a material without detailed knowledge of the band structure. The CuAu alloys are particularly useful in this regard. The effect of the order-disorder transformation on the transport properties of this alloy should be similar to the effect of spin-disorder resistivity on the transport properties of metals with localized magnetic moments.³ We have now extended our earlier work to include the study of dilute amounts of Co, Fe, and Mn in CuAu.

PROCEDURE

The alloys used in this investigation were carefully prepared to insure stoichiometry. The maximum variation in the Cu-to-Au atom ratio was 0.04% as determined by weighing, and the direction of variation was the same in all alloys (all were slightly gold-rich). Au was obtained from Baker and Company, and Cu was obtained from American Smelting and Refining Company. All transition metals were obtained from Johnson-Matthey and Company. Four alloys were prepared: CuAu, CuAu+0.117 at.% Co, CuAu+2.09 at.% Mn, and CuAu+1.01 at.% Fe.

Alloy preparation involved the standard techniques of sealing the constituents in quartz tubes under vacuum, melting, agitating periodically, freezing, and rolling the solidified ingots into wire.

The methods for measuring the resistivity and thermoelectric power for these alloys were previously described.¹

For alloys of the composition Cu_3Au_1 plus dilute amounts of a third component, we write the resistivity as

$$\rho(T) = \rho_{\text{CuAu}}(T) + \rho_i(T), \quad (1)$$

where $\rho(T)$ is the total resistivity of the alloy, $\rho_{\text{CuAu}}(T)$ is the resistivity of CuAu, and $\rho_i(T)$ is the impurity resistivity of the third component.

Resistivity data for the alloys containing Mn and Fe was taken over a period of five days. The alloy containing Co, being more dilute, required ten days to minimize scatter in the data. In Fig. 1, the resistivity of the Co alloy and CuAu are shown. In Fig. 2, the impurity resistivities, ρ_i , for the transition metals are presented. The alloy containing Co has the greatest uncertainty in ρ_i , but appears to agree with the trend to a smaller impurity resistivity immediately above the critical temperature. A drop in impurity resistivity at the critical temperature was also found for Ni in CuAu.¹ It is interesting that a calculation of the Nordheim type⁴ of the change in impurity resistivity due to the

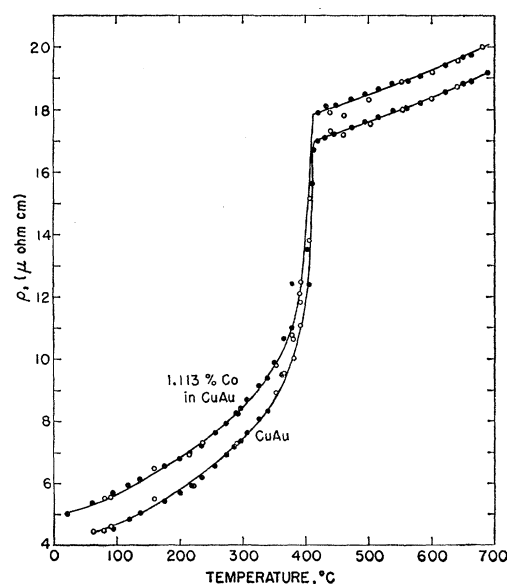


FIG. 1. Resistivities of CuAu and CuAu+Co alloys. The open circles were obtained during heating, filled circles during cooling.

⁴ L. Nordheim, Ann. Physik 9, 641 (1931).

¹ M. D. Blue, Phys. Rev. 117, 134 (1960).

² N. F. Mott and H. Jones, *Theory of the Properties of Metals and Alloys* (Oxford University Press, New York, 1936), p. 310.

³ M. T. Beal, J. Phys. Chem. Solids 15, 72 (1960); P. G. DeGennes and J. Friedel, *ibid.* 4, 71 (1958).

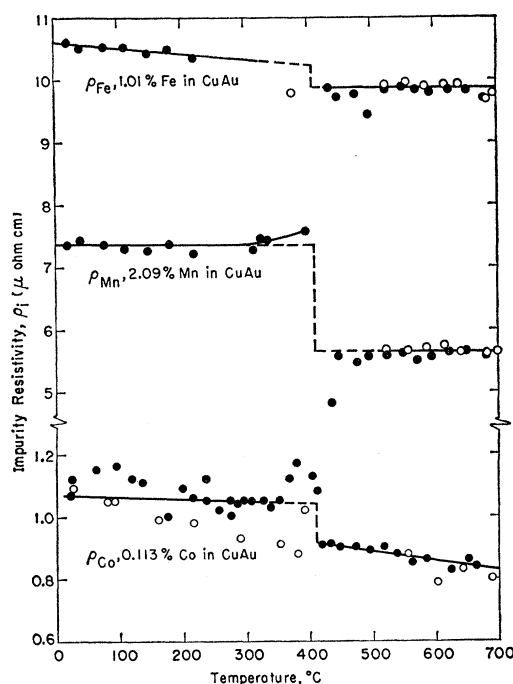


FIG. 2. Impurity resistivity of transition metals in CuAu. Open circles represent data taken after heating; filled circles represent data taken after cooling.

order-disorder transformation gives a result which agrees in sign with experiment. The effect of disorder, in this approximation, is to average the ion-core potential and lower the impurity resistivity for any impurity. The curves for ρ_i in Fig. 2, as drawn, show a transition temperature near 410°C. This was done for convenience in analyzing the data. The transition temperatures lie somewhat lower, and the exact values were not determined.

The thermoelectric powers for these alloys, as determined by a differential method, are shown in Fig. 3. Above the critical temperature, readings could be taken at 24-hr intervals. Below the critical temperature, several days were often required to obtain stable values of thermoelectric power (a linear relation between thermal emf and the temperature difference between the ends of the wires for very small temperature differences). It is possible that the difficulty in obtaining good data in this temperature range was due to the complication of the orthorhombic ordered phase, CuAu II, which is stable above 380°C. Another possibility is the effect of the third component in the CuAu alloy in greatly increasing the time required to attain equilibrium. The thermoelectric power will be sensitive to deviations from equilibrium which should behave in a manner similar to the behavior of additional impurities. Thus the thermoelectric power may be a more sensitive indicator of equilibrium in these alloys than the resistivity.

In some cases below the critical temperature, annealing periods of over one week were not sufficient to re-

produce previous values of thermoelectric power after an intermediate anneal at a different temperature. Therefore, the thermoelectric power is drawn as a dashed line through this region.

ANALYSIS

The thermoelectric power data are analyzed using the relation of Mott and Jones.²

$$Q = (\pi^2 k^2 T / 3 |e|) [d \ln \rho(E) / dE]_{E=E_F} \quad (2)$$

With the alloy resistivity as given by Eq. (1), the thermoelectric power, i , of a CuAu alloy containing a transition metal will be given by

$$\rho Q = \rho_{\text{CuAu}} Q_{\text{CuAu}} + A T \rho_i \lambda_i \quad (3)$$

where Q and Q_{CuAu} are thermoelectric powers of the alloy containing a transition metal and the CuAu alloy, $A = \pi^2 k^2 / 3 |e| = 0.0243$ (ev) (μ/deg), and

$$\lambda_i = \left[\frac{1}{\rho_i} \frac{d\rho_i}{dE} \right]_{E=E_F} = \left[\frac{d \ln \sigma_i(E)}{dE} \right]_{E=E_F} - \frac{1}{E_F} \quad (4)$$

In Eq. (4), the impurity resistivity, ρ_i , has been written in terms of the scattering cross section, σ_i , of the impurity atom, given by free-electron theory as

$$\rho_i = (3h^3 / 16\pi m e^2) (n_i / E_F) \sigma_i \quad (5)$$

In the derivation of Eq. (3) as outlined above, free-electron theory has been assumed to apply to these alloys. These assumptions have been considered previously¹ and are satisfactory above the characteristic temperature for dilute concentrations of impurities.

From the resistivity and thermoelectric power measurements, λ can be determined as a function of temperature for Co, Fe, and Mn in CuAu using Eq. (3) and the smoothed curves of Figs. 1, 2, and 3.

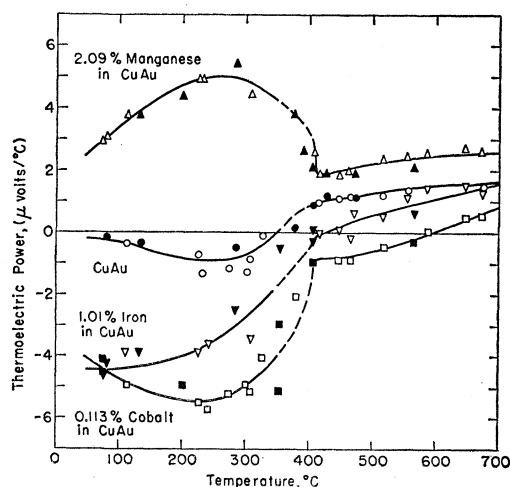


FIG. 3. Thermoelectric power of CuAu alloys containing transition metals. Open symbols represent data taken after heating; filled symbols represent data taken after cooling.

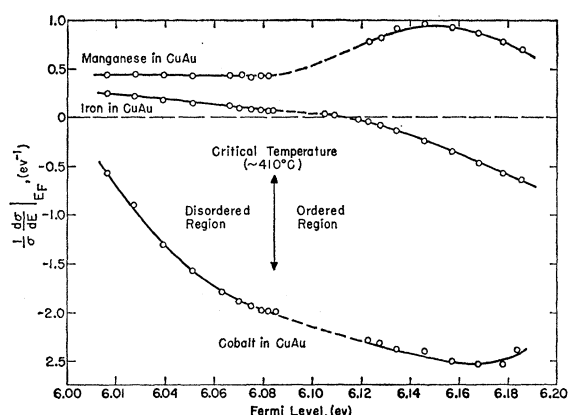


FIG. 4. Variation of $(1/\sigma)(d\sigma/dE)$ for transition metals in CuAu.

λ is found to be temperature dependent. This results from the variation of σ with energy. For a metal, the scattering of electrons at the Fermi energy determines the transport effects. The Fermi energy will depend upon the impurity atom concentration and upon the temperature through thermal expansion. As our impurity concentrations are constant, only the temperature changes the Fermi level, and the actual change may be calculated from the thermal expansion data of Kurnakow and Ageew.⁵ From free electron theory, the Fermi energy of CuAu was calculated to be 6.19 eV at 25°C using the data of Johansson and Linde⁶ for the lattice constant.

From Eq. (4), the variation of $d \ln \sigma / dE$ can now be determined as a function of energy as shown in Fig. 4. At energies corresponding to temperatures just below the critical temperature, the curves of Fig. 4 are shown as dashed lines which correspond to the dashed portion of Fig. 2. The values for λ , calculated from Eq. (3), are subject to large uncertainties in this region for two reasons. Firstly, the value of the products ρQ and $\rho_0 Q_0$ will be subject to appreciable experimental error in this range, and λ is determined from the difference, $\rho Q - \rho_0 Q_0$, which will be subject to greater uncertainty. Secondly, the critical temperature is different for each alloy, and this will introduce a slight error in the application of Eq. (3) which has been minimized by arbitrarily drawing the curves in Figs. 1 and 2 to have the same critical temperature.

The difficulties in analysis should not be unduly belabored, however, as they exist in a relatively small region of temperature. The significance of Fig. 4 is that the scattering parameters, as calculated, are smoothly varying over the temperature range of these measurements.

⁵ N. S. Kurnakow and N. W. Ageew, *J. Inst. Metals* **46**, 481 (1931).

⁶ C. H. Johansson and J. O. Linde, *Ann. Physik* **25**, 1 (1936).

DISCUSSION

Our experiments on resistivity and thermoelectric power in CuAu alloys have been analyzed using free electron theory. The impurities have been treated as independent scatterers, and their contribution to the resistivity has been assumed additive at all temperatures. These assumptions may be justified by showing that the results are in agreement with those of similar experiments on other noble metal alloys. Values for the atomic resistivity increase for Ni, Co, Fe, or Mn in CuAu are found to be 2.4, 10.0, 9.4, and 3.5 in units of $\mu\text{ohm cm}$ at 0°C, where the value for Ni is taken from our previous work. These results compare quite well with results for Cu- and Au-based alloys as summarized by Gerritsen.⁷

All thermoelectric power curves show a break at the transition temperature, T_c , which corresponds to a discontinuity in $(d\rho/dT)_{T=T_c}$, a result to be expected if Eq. (2) is valid. The values of $d \ln \sigma / dE$ for transition metals in CuAu may be compared to the work of Domenicali on Cu-based alloys.⁸ It is seen that for the transition metals in either a Cu or a CuAu matrix, $d \ln \sigma / dE$ has a negative minimum (at approximately -5) for Ni and increases monotonically with decreasing atomic number, becoming positive for Mn. A similar trend occurs in alloys of the transition metals with Au as a solvent.⁹

This result may be represented by the following physical model. The effect of the impurity is represented by a potential well of appropriate shape. The depth of the well increases through the series Ni, Co, Fe, and Mn. The total scattering cross section of the well, and the derivative of the total cross section with energy vary rather smoothly with well depth. For a given element, the depth depends (a) on the solvent, and (b) on the temperature. In this way, an element in Au (for example, Fe) at high temperature can resemble, in its effect on transport properties, an adjacent element in the series (in this case, Mn) at lower temperatures in Cu.

For our CuAu alloys, the principal scattering mechanisms of atomic vibrations, atomic disorder, and impurities are additive in their contribution to the electrical resistance. The order-disorder transition appears to influence the impurity scattering only through the small discontinuous change in total cross section and a change in the Fermi level due to lattice expansion. We thus conclude that within the experimental limitations of our measurements, the assumptions of free-electron theory and a simple model of impurity scattering will explain the rather complex thermoelectric behavior of these alloys.

⁷ A. N. Gerritsen, *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 19, p. 210.

⁸ C. A. Domenicali, *Phys. Rev.* **112**, 1863 (1958).

⁹ See, for example, J. Friedel, *Can. J. Phys.* **34**, 1190 (1956). In Friedel's analysis, the quantity Δx is identical to $-E_F \lambda$ as used in this work.