

Solute Clustering and Magnetic Behavior in Au-Fe[†]

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A solid solution of Au-Fe was given various heat treatments causing the Fe to cluster. This variation in short-range compositional order induces corresponding changes in the magnetic behavior of the alloy. Especially noteworthy was the response of the temperature dependence of the magnetic order. There appears to be a gradual change in the nature of the exchange interaction which attains short-range character with increased clustering. The Mössbauer effect was used to observe this gradual transition by measuring the magnetic hyperfine splitting of the ⁵⁷Fe.

Recently there have been several investigations¹⁻⁹ of the clustering of magnetic solutes in a diamagnetic solvent. However, none of them, except those reported in Refs. 1, 3, and 9, have been conducted at constant composition. In all of the other investigations, the so-called clustering was the direct result of the statistical fluctuation in composition nearly corresponding to the high-temperature equilibrium distribution of solute. In most cases, these studies have varied the bulk composition and interpreted the results in terms of the attendant variation in the local composition, which carries with it the assumption that the exchange interaction is necessarily short range. By holding the bulk composition constant and varying only the short-range compositional order, a means can be provided for directly observing the effects of clustering while obviating the assumption of short-range exchange forces. Ryan and co-workers¹ deliberately induced the clustering of Ni in Ni-Co alloys by neutron irradiation, whereas Kussman and Wollenberger³ used both cold work and varying heat treatment to induce variation in short-range order. We have annealed Au-Fe to produce variations in short-range order and then observed the corresponding variation in magnetic properties by means of the Mössbauer effect.

A single, isotopically enriched solid solution of 16.6 at. % Fe in Au was given three sequential heat treatments: quenched from 920 °C into ice water; annealed for 4 days at 383 °C; and annealed for 5 days at 225 °C. Both annealings were made at temperatures well within the two-phase region. This alloy is a single-phase α solid solution that is a random antiferromagnet below its characteristic ordering temperature.¹⁰ It was used as an absorber, and Mössbauer spectra, ranging from room temperature to 4.6 °K, were obtained after each treatment. Figure 1 contrasts the spectra of the annealed and quenched states, both obtained at 65 °K. The quadrupolar split spectra of the quenched specimen remains essentially unaltered at higher temperatures. The annealed state gives

clear evidence of magnetic hyperfine splitting that was totally lacking in the quenched specimen. All spectra correspond to a single crystallographic phase. However, gross fluctuations in composition have been produced, as attested to by the drastic change in the temperature dependence of the magnetic hyperfine splitting as shown in Fig. 2.

The important features of this experiment, as revealed by Fig. 2, are that (a) the magnetic hyperfine splitting commences at proportionately higher temperatures with increased annealing, and that (b) in the annealed condition, there is no sharp transition from the paramagnetic to the ordered state, as there is in the quenched state. In addition, it was discovered that no detectable increase in the hyperfine splitting at 4.6 °K or change of isomer shift was produced by annealing.

The observations reported here are consistent with the following model, by no means novel but perhaps never before so well substantiated: As a consequence of the annealings there exist a continuum of hypervolumes of continuously varying composition, and associated with each is a specific composition and a unique ordering temperature. It should be remarked that the state of continuously varying composition is an experimental inference based on the continuous manner in which the hfs varies (Fig. 2). Also, it should be remembered that classical nucleation and growth theories of phase transformation would predict two or, at most, three discrete compositions. However, in the present case, there is an observable distribution of the ordering temperature with an ever increasing fraction of the Fe becoming magnetically ordered as the ambient temperature is lowered.

Although in the absence of an external field Au-Fe of this composition appears to be over-all antiferromagnetic, in the presence of a "strong" magnetic field, viz., 50 kOe, the Mössbauer spectrum is completely polarized.¹⁰ On the other hand, theoretical calculations suggest that Fe nearest neighbors are ferromagnetically coupled and that an alloy containing approximately 17 at. % Fe should

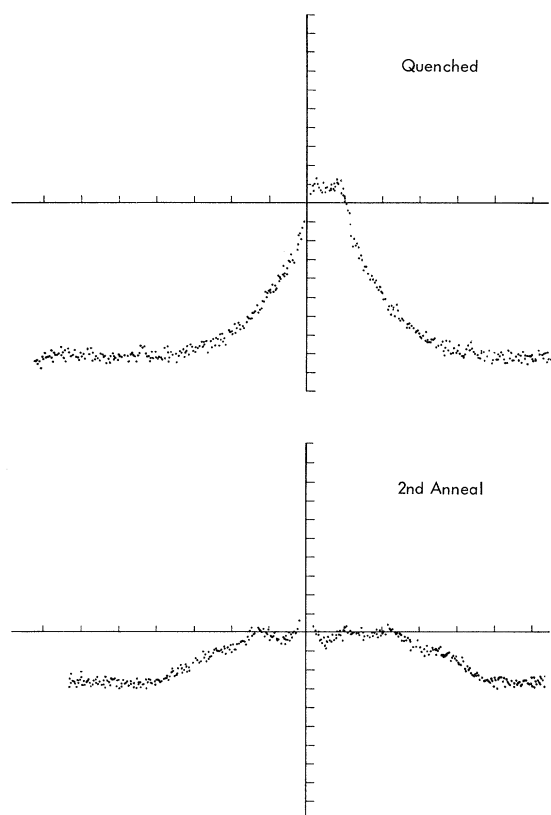


FIG. 1. Spectra from the annealed and quenched states showing the effect of clustering. Both spectra were obtained at 65°K.

be entirely ferromagnetic.¹¹ Until both magnetization as well as polarization measurements are completed on the annealed or clustered state, it is impossible to state with certainty the sign of the exchange interactions between atoms within the clusters and between the clusters themselves. However, the results are consistent with the predictions of Brout,¹² whose theory is based upon short-range ferromagnetic exchange forces (see Fig. 3). The experimental situation varies from the predominance of short-range coupling at relatively high temperatures between the iron-rich clusters to the ordering of the iron-poor remainder at lower temperatures. (The exchange interaction can be extremely long range in Au-Fe at sufficiently low temperatures; e.g., Au-1 at. % Fe orders at approximately 4°K.) Thus, it is not surprising that the annealed specimens give results that lie between the Brillouin function, which is strictly the result of long-range forces (Fig. 3), and the calculations of Brout, which are derived solely from short-range forces.

A similar investigation⁹ of Ni_{0.45}Cu_{0.55}, spiked with ⁵⁷Co and used as a source, produced results

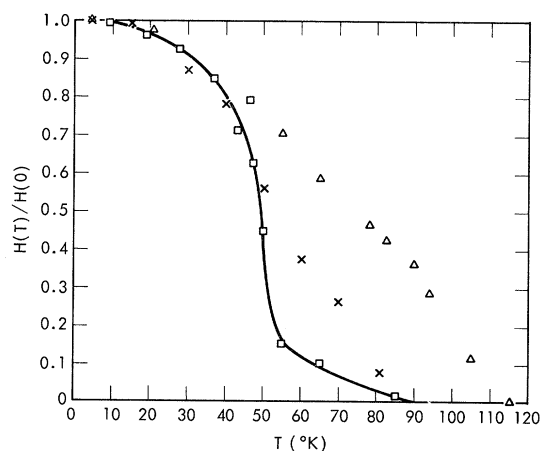


FIG. 2. Plot of the reduced value of the effective hyperfine field vs temperature. Note that the splitting begins at relatively higher temperatures in the annealed state and continues without the inflection demonstrated by the quenched condition. Open square, quenched; cross, annealed 4 days at 383°C; open triangle, annealed 5 days at 225°C.

that were superficially similar to those reported here for Au-Fe, viz., a low-temperature anneal raised the temperature at which magnetic order

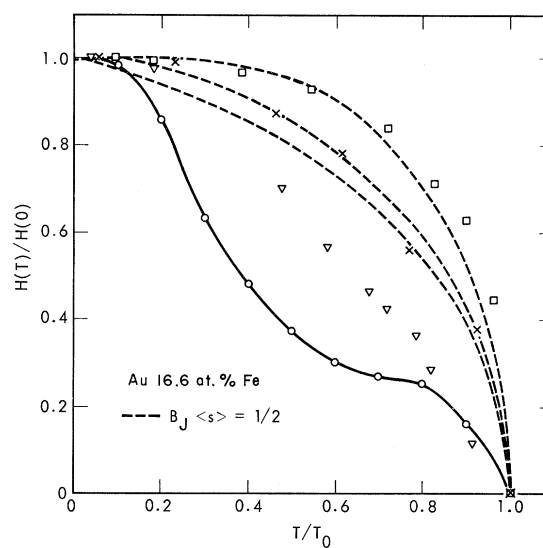


FIG. 3. Reduced value of the effective hyperfine field, plotted as a function of reduced temperature. T_0 is taken to be the temperature at which the first detectable line broadening occurs. Note that the quenched specimen demonstrates long-range coupling by approximating the Brillouin function, whereas the clustered state produces results that tend toward the predicted curve for strictly short-range interactions. Open square, quenched from 900°C; cross, annealed 4 days at 383°C; open inverted triangle, annealed 5 days at 225°C; open circle, Ref. 13.

commences. However, an important difference exists between the two systems in that the ordering of CuNi as a function of (T/T_0) is unaltered by the annealing treatment. We may hypothesize that at the concentrations used, i. e., $(\text{Ni})/(\text{Cu}) \approx 1$, the low-temperature anneal produces a departure from randomness in the "long-range" compositional order which alters the strength of the exchange interaction but leaves the exchange forces long range in character in all cases.

Most of the previous investigations of clustering

have been on Ni-Cu and have employed classical magnetization measurements. The large paramagnetic moments, e. g., $8-10 \times 10^{-6} \mu_B$, are generally interpreted as magnetically coupled clusters of Ni. Magnetization measurements on Au-Fe combined with heat treating would be of value. At present, it can be said only that Mössbauer experiments below the ordering temperature suggest the presence of iron-rich magnetically coupled clusters, with a continuum of magnetic ordering temperatures.

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Multiplet Splitting of the 4s and 5s Electrons of the Rare Earths

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The multiplet splitting of 4s and 5s electrons of trivalent rare-earth ions has been measured by photoelectron spectroscopy. This splitting represents the energy difference between the s-electron spin-up and spin-down final states.

Photoelectron lines arising from the s shells of rare-earth (RE) ions should be split by the interaction of the s shell with the partly filled 4f shell. Such splitting, called the multiplet splitting, has been observed previously¹ in the 3d elements. We report here the first observation of this splitting in the rare earths, and measurements of its magnitude for the 4s and 5s shells of a number of these elements. A simple approach is used to explain the major part of the Z dependence of the splitting.

The x-ray photoelectron² measurements were carried out with a Varian IEE-15 spectrometer, using Mg K α radiation. The instrumental resolution yielded a linewidth of 1.65 eV on the Au(4f) or graphite C(1s) lines. The samples, all RE trifluorides, were in the form of freshly crushed crystalline powders mounted with double-sided adhesive tape. Since we are here concerned only

with line splitting, no attempt was made to determine the magnitude of the charging effect. However, the fact that lines of instrumental width were obtained for the F(1s) electrons in these materials indicates that charging effects do not contribute to the linewidths.

A major concern in all x-ray photoelectron spectra (XPS) measurements is the condition of the 10-30-Å surface layer which is actually under observation. Many materials, especially metals, are covered by an oxide layer of almost this thickness after exposure to air. Other materials, e. g., (RE)₂O₃, adsorb large quantities of water. Fortunately the XPS technique makes it possible to determine the chemical composition of the layer under investigation. In the samples reported here the O(1s) line, indicative of adsorbed H₂O, or partial conversion to oxide, hydroxide, or carbon-