PHYSICAL REVIEW B VOLUME 8, NUMBER 9 1 NOVEMBER 1973

Susceptibility of Co Impurities in Cu-Al Alloys†

J. Bensel and J. A. Gardner

Laboratory for Research on the Structure of Matter and Department of Physics, Philadelphia, Pennsylvania 19174

(Received 14 March 1973)

The susceptibility of dilute Co impurities in liquid Cu-Al alloys has been measured over the entire host composition range. We find a smooth transition from a "nearly magnetic" impurity state in the pure-copper host to a nonmagnetic state in pure aluminum. The Co susceptibility is reduced by more than an order of magnitude, and its slope with temperature changes sign between the pure copper and pure aluminum hosts. The results indicate that in hosts containing less than 40-at.% Cu, the Co impurity state may be described by a nonmagnetic density-of-states model with perturbative spin-fluctuation corrections. For higher-copper-concentration hosts, spin fluctuations become rapidly more important, and perturbation corrections are probably insufficient.

INTRODUCTION

Dilute transition-series impurities in normal metals can display a wide variety of magnetic properties. The most magnetic of the 3*d* transition elements are Cr, Mn, and Fe. When dissolved in noble metals, these three are "strongly magnetic" in the sense that their susceptibility varies inversely with temperature and is of the same order of magnitude as that of the free ion, but these same impurities in polyvalent normal metals have a temperature-independent "nonmagnetic" susceptibility below 300 °K. This striking transition from a magneticlike to a nonmagneticlike state when the host-conduction-electron density is increased by only about a factor of 2 has been the subject of a great deal of interest during the past few years. In one group of experimental studies,[1–3] a continuous transition from magnetic to nonmagnetic behavior has been observed for these three impurities in liquid-host alloys containing varying ratios of a noble metal and aluminum. From a theoretical point of view, however, the transition to a nonmagnetic state is incomplete in these systems, because even in an aluminum host, the "nonmagnetic" susceptibility of Cr, Mn, and Fe is too large to be described unambiguously by a simple density-of-states model. In order to observe a transition into an unambiguously nonmagnetic state, we have undertaken an investigation of the magnetic properties of Co impurities in liquid copper-aluminum alloys. In this paper we give the results of our susceptibility measurements on this system.

In general a cobalt impurity is less magnetic in a given host material than Cr, Mn, or Fe. Isolated Co impurities in pure copper have a nearly constant susceptibility below 300 °K.[4] At higher temperature, however, the susceptibility follows a Curie–Weiss behavior and is nearly as large as that of more magnetic impurities.[5] We find a smooth transition from this nearly magnetic state of Co in copper to a nonmagnetic state in liquid aluminum. The susceptibility of Co in liquid aluminum is quite small, about seven or eight times the aluminum Pauli susceptibility, and, characteristic of all impurities in liquid trivalent metals,[6–8] it is a strongly increasing function of temperature. In a preliminary report of this and nuclear-resonance work in the aluminum-rich host alloys,[9] we showed that the *Al*Co impurity state can be well described by a simple density-of-states model with an impurity bandwidth of about 3 eV. The Co susceptibility in Al can be divided into orbital and spin parts, and it is straightforward to show that the enhancement of the spin susceptibility by spin-fluctuation perturbations is less than 50%. The combined resonance-susceptibility results allowed us to establish that the anomalous temperature dependence of the liquid-state Co susceptibility is due to a temperature dependence of the impurity density of states. The reason for this strong increase with temperature is not well understood at this time, but we have found it to be a useful experimental tool for studying the impurity state. In effect, we can alter the impurity density of states in a given experimental sample by 20% or more over the range of temperature experimentally available. If the resulting change in magnetic properties can be measured with sufficient accuracy, one can determine the impurity density of states, the orbital and spin susceptibility, and the enhancement by spin fluctuations. For this reason, we have taken great care to measure the Co susceptibility and its temperature dependence as accurately as possible.

EXPERIMENTAL RESULTS

The susceptibility of Co in liquid aluminum is shown in Fig. 1 for three Co concentrations. χ_{Co} is defined by

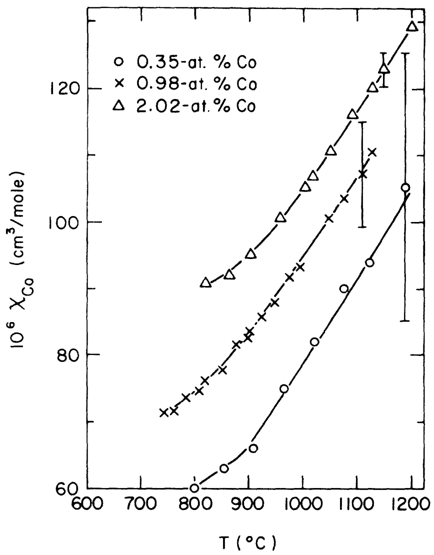

FIG. 1. Susceptibility of Co in liquid Al. χ_{Co} is defined by Eq. (1) of the text. Error bars indicate experimental uncertainty in the magnitude of the susceptibility.

$$\chi_{Co} = [\chi_A - (1-c)\chi_H]/c \, , \tag{1}$$

where χ_H, χ_A are the molar susceptibilities of the host and the host with concentration c of Co, respectively. In Fig. 2, the Co susceptibility in the copper-aluminum host alloys is shown vs host composition. The cobalt concentration was 1 at.% in all cases shown. The scale in the copper-rich hosts is compressed by a factor of 20 because of the rapid divergence of χ_{Co} near the middle of the host-concentration range. Our measurements of the host susceptibilities are in good agreement with previously published results[1] and are not shown. In the absence of impurity interactions, the Co susceptibility defined by Eq. (1) should be independent of Co concentration. In general, we found that it increases somewhat with c, but the absolute uncertainty (discussed in the following section) is too large to determine the concentration dependence quantitatively. The relative dependence of χ_{Co} on c, which is shown in Fig. 1, is typical of all host alloys.

Above 800 °C, the precision of the susceptibility measurements in a given sample is limited only by a small random weighing error, and the temperature dependence of χ_{Co} can be determined quite accurately. In the Al-rich hosts, the Co susceptibility becomes linear in temperature above 950 °C, and in the Cu-rich hosts it is linear over the entire temperature range studied. In Fig. 3, $d\chi_{Co}/dT$ at 1100 °C in samples containing 1-at.% Co is shown vs host composition. To facilitate comparison of the results, the slope is normalized to χ_{Co} (1100 °C) given in Fig. 2. The error bars in Fig. 3 do not include the uncertainty in the normalization, however, but reflect only the uncertainty in the slope. In the Cu-rich host alloys, the data can be fit equally well to a linear or a Curie-Weiss temperature dependence. In these hosts the liquidus point is rather high, and the available temperature range in the liquid state is only about 100 °C. The best fit to a $(T+\Theta)^{-1}$ dependence for the 1-at.% *Cu*Co sample gives $\Theta = 900 \pm 200$ K.

In the Al-rich host alloys the slope of χ_{Co} in the

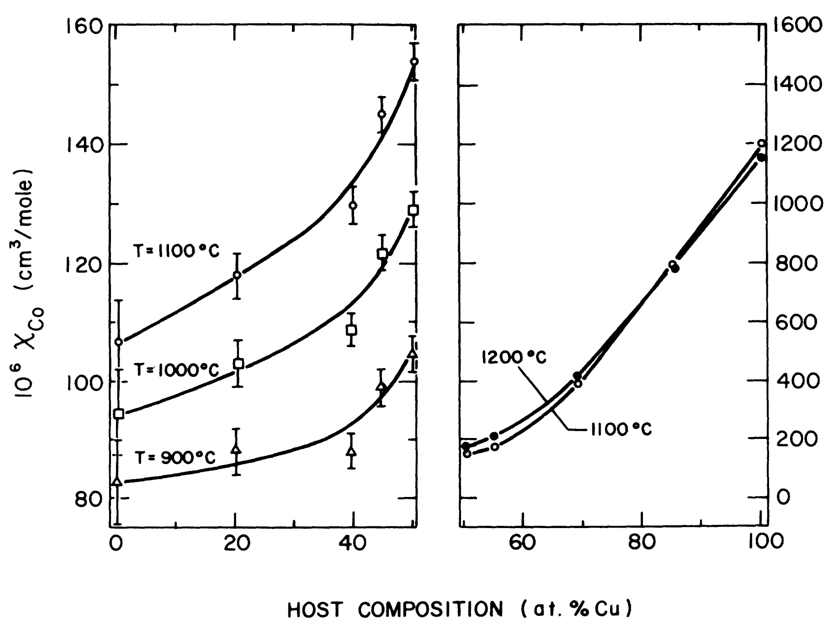

FIG. 2. Susceptibility of Co in liquid Cu-Al alloys containing 1 at.% Co.

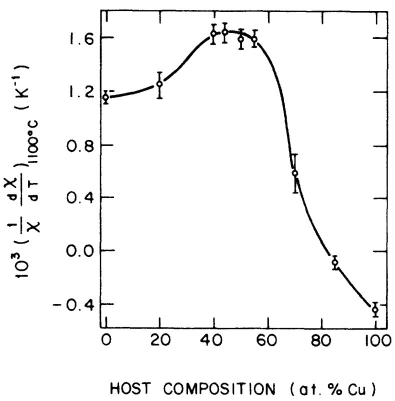

FIG. 3. Relative slope of Co with temperature. The susceptibility to which the slope is normalized is taken from Fig. 1.

high-temperature region was independent of Co concentration for all samples studied. The Co concentration was limited to less than 2 at.% except for host alloys of 44 and 50-at.% copper in which the susceptibility was measured in samples containing as much as 5-at.% Co. In these samples $d\chi_{Co}/dT$ at all concentrations agreed well within the experimental scatter of about 5%. Some concentration dependence of $d\chi_{Co}/dT$ was found in pure copper hosts, however. In a 4-at.% *Cu*Co sample, the slope was 20% larger in magnitude than in a 1-at.% sample, corresponding to a Weiss temperature of only 400 ± 200 K.

EXPERIMENTAL PROCEDURE

The apparatus used for this work is a much improved version of a Faraday balance system described previously.[1] The balance now used is an Ainsworth vacuum digital microbalance having a precision of 20 μg. Sample oxidation during prolonged measurement periods was completely negligible, and the accuracy with which the absolute Co susceptibility could be determined was limited by the reproducibility of the sample-holder and host-alloy susceptibility. Below about 800 °C, the sample-holder susceptibility became progressively less reproducible, and often displayed some temperature hysteresis. Above this temperature, the only significant error was a small temperature-independent irreproducibility introduced when the sample holder was removed to add host metals or Co. This error limits the accuracy of χ_{Co}, but does not affect its slope with temperature.

The temperature was measured with a thermocouple positioned a few millimeters below the sample. In order to avoid large thermal-lag errors, it was necessary to allow the sample and furnace to reach equilibrium before weighing, but when proper precautions were taken, errors in the temperature were negligible.

All alloys were made *in situ* in order to minimize uncertainty in Co concentration. We followed the prescription of measuring the susceptibility of the alumina sample holder, the sample holder plus host, then the holder, host, and Co. The alloys were allowed to homogenize for several hours at 1100 to 1200 °C before measurements were made. No temperature hysteresis was found, and chemical analysis of alloys made by this technique shows no significant inhomogeneity.

CONCLUSIONS

The behavior of the Co susceptibility as a function of host composition indicates that the Co remains nonmagnetic up to a copper concentration of about 40 at.%. Beyond this composition, the Co susceptibility begins to diverge, and its temperature dependence begins to change character. Because of the impurity density-of-states temperature dependence, the slope of the Co susceptibility with temperature is positive in the Al-rich host alloys, but decreases and eventually becomes negative near the pure-copper-host composition. There has been a great deal of theoretical effort devoted to nonmagnetic and spin-fluctuation models of the impurity state, and this system appears to be a fertile area for application of such theory. In particular, it is clear that in hosts containing less than 40-at.% copper, low-order perturbative corrections for spin-fluctuation enhancement of the susceptibility should be adequate, and it should be possible to determine all model parameters experimentally. The center of the host composition range evidently marks the onset of stronger temperature-dependent spin fluctuations, and it may be possible to determine experimentally both the magnitude and temperature dependence of the spin-fluctuation susceptibility enhancement. We are presently pursuing these interesting possibilities in a nuclear-resonance investigation of this impurity system. These results will be published later.

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†Supported by the National Science Foundation through the Laboratory for Research on the Structure of Matter, and the Advanced Research Projects Agency.

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