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NUCLEAR MAGNETIC RESONANCE AND INTERNAL OXIDATION OF Cu-Mn ALLOYS

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It is shown that vacuum annealing of comminuted Cu-Mn alloys can cause loss of Mn solute by a mechanism of internal oxidation. Some loss of Mn solute can even occur in the process of comminution. Order of magnitude errors in the true Mn solute concentration can result, leading to erroneous conclusions concerning internuclear reactions and quadrupole effects as derived from nmr measurements.

Nmr parameters of Cu-based binary alloys have been explained in terms of direct and indirect internuclear reactions and quadrupole perturbations.[1-4] Most studies in this area have been made on unannealed material containing unspecified amounts of cold work.[6-11] For binary alloys containing sufficient solute to produce second-order quadrupole interactions throughout the Cu lattice, first-order quadrupole effects arising from cold work should not be observable. In such cases, the nmr line widths, intensities, and Knight shifts, should not change with annealing heat treatment. For solute concentrations below approximately 1 at.%, first-order perturbation effects are in evidence and the effect of cold work on the nmr parameters is of significance. In this region the effect of annealing heat treatment on nmr parameters can be considerable.

Two authors, in particular, have examined the effects of heat treatment of the nmr of Cu-based alloys. Rowland[12] used samples that were generally not annealed, but he observed that, in the few (unspecified) instances when filings were annealed, the resonance intensities before and after annealing were unchanged. Chapman and Seymour,[13] however, observed that some features of the Cu^{63} resonance in Cu-Mn alloys, containing a few wt% of Mn, were widely different, depending on whether the samples were powder as filed or powder which had been annealed in vacuo at 400°C for four hours. The annealed samples showed a narrowing of the line width, an increase in the intensity, and a reduction in the Knight shift. These authors observed no significant changes for annealed Cu-Ni samples, except for a slight narrowing of the line in all cases. They further observed that a second anneal had no further effect on the Cu-Mn resonances. They therefore proposed that heat treatment produces a cluster of Mn ions, thus leaving the bulk of the material free from local fields. They were unable to confirm this hypothesis by x-ray detection of free Mn, but used this cluster concept to interpret their nmr results obtained from annealed Cu-Mn samples.

It is the purpose of this Letter to disclose that a detailed study of powdered Cu-Mn alloys has established that changes in nmr line widths, intensities, and Knight shifts can result from loss of the Mn solute concentration by internal oxidation[14] of Mn. X-ray analysis determined that the only significant second phase present in vacuum annealed Cu-Mn samples was cubic MnO in the form of manganosite.[15] Selected area diffraction measurements in the electron microscope on internally oxidized bulk material confirmed this result. No evidence for free or clustered Mn could be detected. Samples were prepared by high speed cutting,[16] grinding,[17] and by hand filing. All exhibited internal oxidation effects. High speed cutting of Cu-Mn alloys in atmospheres of N_2, H_2, NH_3, and Ar did not prevent oxidation of a portion of the solute Mn during vacuum annealing. Samples cut under liquid N_2 also showed internal oxidation effects on vacuum annealing. The source of oxygen presumably lies in adsorbed oxygen or copper oxide formed during, or after, comminution of the alloy.

Comminuted Cu-Mn samples were placed in small quartz containers, evacuated to 7.5×10^{-2} Torr, and sealed. The nmr parameters were then measured as a function of annealing time at 400°C. The concentration of unoxidized solute Mn remaining in the Cu lattice after a given vacuum anneal was determined by precision x-ray measurements. The residual solute concentrations of Mn in the Cu lattice were found to correlate closely with the observed resonance intensities, line widths, and Knight shifts obtained from the annealed samples.

A typical loss of solute from a 400-mesh sample of Cu-Mn alloy, of bulk starting concentration 1.97 wt% Mn, is shown in Fig. 1, as a function of total vacuum annealing time. After repeated vacuum annealing at 400°C this sample contained a residual Mn solute concentration of only 0.10 wt%. The nmr parameters of the Cu^{63} resonance line changed, with loss of solute, accordingly. The amount of MnO formed (and hence the solute concentration of Mn remaining in the lattice) apparently equilibrates with the amount of oxygen present in the closed system. Samples annealed in an atmosphere

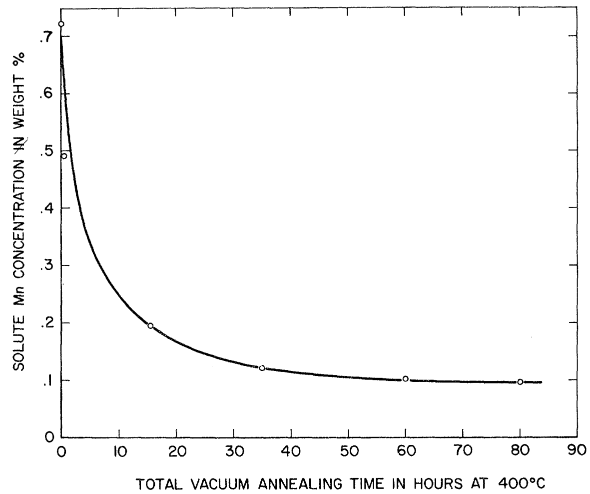

FIG. 1. Typical loss of Mn solute from a 400-mesh Cu-Mn powdered sample as a function of total vacuum annealing time.

of hydrogen gave a similar result. Examination of the kinetics of Mn oxidation shows this result to be expected.

Diffusion calculations were made, based on the known diffusion rate of oxygen in a Cu lattice at the annealing temperature. The calculated time constants for oxygen diffusion are in agreement with the experimentally observed time constants for loss of Mn solute.

Internal oxidation effects were found to be present in several transition-metal solutes in Cu. They were particularly apparent in solutes of Mn, Ti, and Fe.[18] Some oxidation effects were also observed with Al in Cu.

If an oxide of the solute can be formed which is more stable than the oxide of the host lattice, then some loss of solute can be expected to result from annealing the sample in vacuo. The result shown in Fig. 1 also indicates that loss of solute by internal oxidation can occur during the process of comminution of the sample. Both annealed and unannealed samples can therefore lead to errors, if measured parameters are correlated directly to solute concentrations obtained from chemical analysis. Resonance results based on the true solute concentration of annealed samples of Cu-Mn (and other solutes) have been interpreted on the basis of internuclear reactions and quadrupole effects. Full details of these findings will be presented elsewhere.

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ISOTOPE EFFECT IN SUPERCONDUCTING ZINC*

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The isotopes of a superconducting element are known to have zero-field transition temperatures T_c which vary with isotopic mass M such that $T_c \propto M^{-z}$. The model of Bardeen, Cooper, and Schrieffer (BCS)[1] predicts a value of 0.5 for z for all elements. Although data for some elements support a value of 0.5 for z, data for other elements suggest substantial deviations from this value. Models proposed by Swihart (S),[2] Morel and Anderson (MA),[3] and Garland (G)[4,5] predict $z = 0.5(1-\xi)$, in which ξ depends on the element.

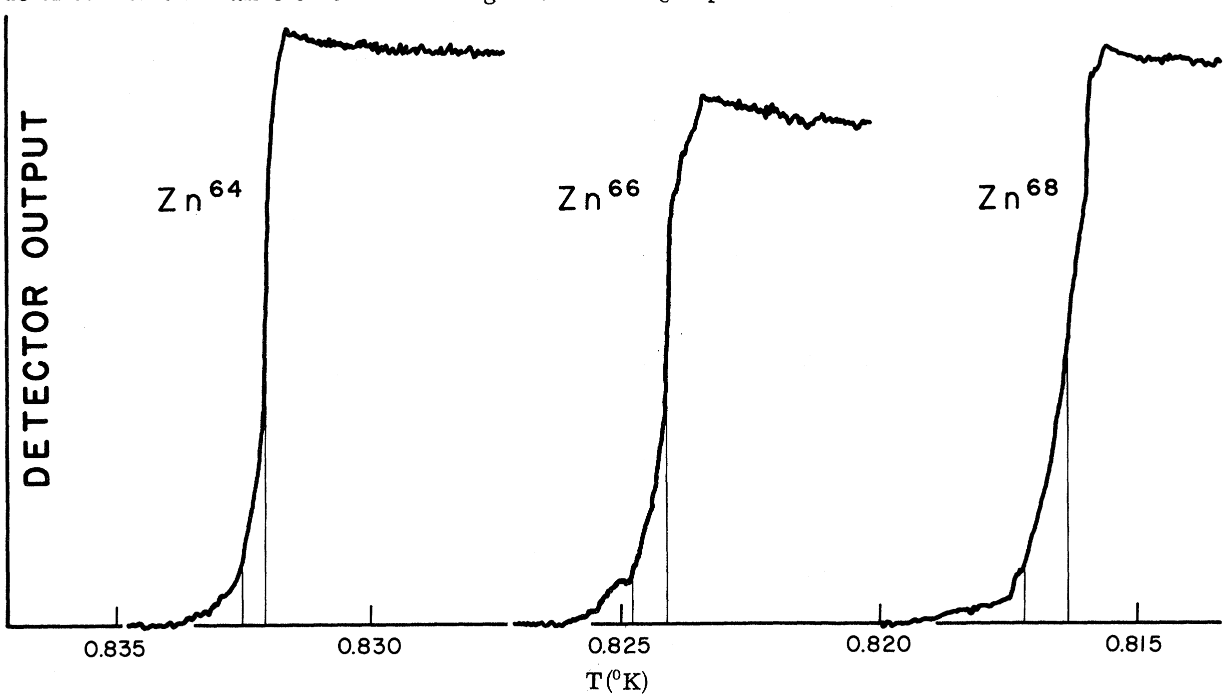

FIG. 1. Superconducting-to-normal transitions of isotopes of Zn in a magnetic field of 2.53 Oe. Ordinates are outputs of a mutual induction detection system. Vertical lines are drawn to points on each curve at which the output of the detector had decreased by 50 and 90% of its maximum change.