

Brief Reports

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^{63}Cu Knight shift in an alloyed Cu-Zn system prepared by mechanical alloying

Li Bai-Qin and Wang Ye-Ning

National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University,
Nanjing 210008, People's Republic of China

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The characteristic variations of the ^{63}Cu Knight shift in the mechanically alloyed Cu-Zn system with Zn content are presented and reasonably identified. The difference of the ^{63}Cu Knight shift in the α -phase Cu-Zn alloy from that in pure copper is proportional to the number of Cu nearest neighbors which are Zn. Through comparison with earlier NMR results on melt-alloyed brasses, reliable results and analyses are given for the α phase.

The Cu-Zn alloy system (brass) is of great technological interest and has provoked a large number of theoretical investigations to calculate electronic properties of the various crystallographic phases.^{1,2} In addition to being made by conventional alloying techniques, the Cu-Zn alloys can be prepared by mechanical alloying (MA) of the powder blends of constituent metals with specific advantages, particularly to obtain a series of intermediate alloyed states during alloying.^{3,4} As shown in Ref. 4, the information about subtle changes of the chemical short-range order (CSRO) associated to the series of intermediate alloyed states is important for modern theoretical calculations and for revealing the mechanism of MA. It can be detected by ^{63}Cu nuclear magnetic resonance (NMR) since NMR differs from x-ray diffraction (XRD) in being sensitive not only to local, as opposed to long-range, symmetry but also to the electronic structure and the atomic configurations present in metals on a local scale within 0.5–1-nm radius through probing the interactions between the nuclear moments and their surroundings in metals.^{5,6} In order to monitor the MA process of the Cu-Zn system from the microscopic aspect by NMR, it is necessary to give reliable identification of the ^{63}Cu peaks because no NMR measurements on mechanically alloyed samples have been reported by others so far except for $\text{Cu}_{59}\text{-Zr}_{41}$ blends.⁷ On the other hand, Bloembergen and Rowland⁸ (BR) have reported that in α -phase Cu-Zn alloys the ^{63}Cu resonance frequency is independent of composition and the ^{63}Cu NMR becomes unobservable for Zn contents in excess of 20% at room temperature (RT), but in liquid Cu-Zn alloys a linear decrease of the relative ^{63}Cu Knight shift with Zn contents is observed by Odle and Flynn,⁹ and in the analogous Ag-Cd system the Knight shifts of both Ag and Cd resonances in the α phase decrease continuously as the Cd content is increased.¹⁰ So the characteristic variations of the ^{63}Cu Knight shift in α -phase Cu-Zn alloys need to be studied in more detail.

The mechanically alloyed samples of $\text{Cu}_{100-x}\text{-Zn}_x$

(at. %) where $0 < x < 68$ were prepared under the same conditions as reported in Ref. 4. The ^{63}Cu ($I = \frac{3}{2}$) NMR measurements were performed on a Bruker MSL-300 high-power pulsed Fourier-transform NMR spectrometer equipped with a 7.05-T superconducting magnet at RT. A Hahn echo two-pulse sequence, incorporating the phase cycling described by Kunwar, Turner, and Oldfield¹³ was used to suppress the free-induction decay and ringing artifacts. Extensive subsidiary experiments were conducted to determine the best NMR parameters. The radio-frequency (rf) pulse lengths are $1.8 \mu\text{s}$ and the delay between the two pulses is $20 \mu\text{s}$. The power of the rf pulses was adjusted to obtain the largest amplitude of the echo. It is seen in our measurements that the ^{63}Cu signal undergoes a sharp reduction, about two orders of magnitude, for the samples that are ball milled over 2 h when some of the Zn are alloyed with Cu.⁴ This result agrees with that found by BR. According to the signal-to-noise ratio, NMR data represent the signal averaging

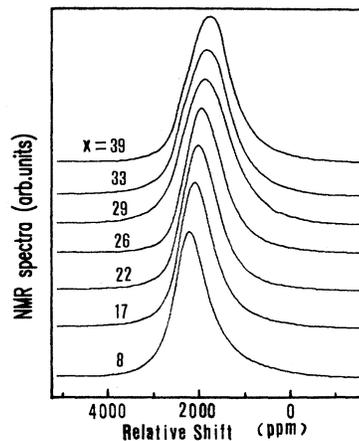


FIG. 1. Some of the typical ^{63}Cu NMR spectra for alloyed $\text{Cu}_{1-x}\text{Zn}_x$.

of 10 000 or more scans. The delay time between scans is 70 ms.

The ^{63}Cu NMR spectra, shown in Fig. 1, were obtained from the Fourier transform of the second half of the solid echo. It has been demonstrated in Ref. 4 that the signals arise from the central line ($\frac{1}{2} \leftrightarrow -\frac{1}{2}$), whereas the satellite transitions are broadened beyond detectability. The Knight shift is sensitive both to bulk properties of the host lattice and to the charge-density distribution due to the local environment around the probe nuclei. Because of the random composition fluctuations in a solid solution of Zn in Cu, the Knight shift of those ^{63}Cu nuclei with greater or smaller numbers of Zn atoms nearby may differ from the shift characteristic of the most probable nearby composition. It is expedient to assign a unique Knight shift to a particular most probable composition and attribute the observed linewidth to the microscopic fluctuations in composition and to quadrupole broadening effects. The variations of the relative Knight shift values K determined by using the line center (peak) of the ^{63}Cu resonance externally relative to the preferred reference compound CuBr,⁵ against Zn content, are presented in Fig. 2 for the mechanically alloyed Cu-Zn system after ball milling of 12 h. The XRD patterns of these samples confirmed that the crystallographic structure is almost identical with that in Cu-Zn brass,¹⁴ i.e., alloys with less than 39 at. % Zn were fcc and alloys containing 40 to 57 at. % Zn were mainly bcc. The lattice parameter of all phases estimated from the XRD peaks is also in agreement with that of brass for the same composition.¹⁴ The lattice-parameter changes for the fcc phase versus Zn content, plotted in Fig. 3, suggest that the fcc phase is a solid solution of Zn in Cu because the Cu atom has a smaller atomic radius than that of Zn and the increase in the lattice parameter can be explained as the result of dissolution of Zn into the Cu lattice.

Combined with the XRD data, it can be reasonably recognized that the ^{63}Cu Knight shift in the β , γ phases are about $0.15 \pm 0.01\%$ and $0.07 \pm 0.01\%$, respectively (Fig. 2). The present value of K for alloys containing 49 at. % Zn, 0.153%, is in good agreement with that given by Sagalyn and Hofmann¹¹ and close to that of West¹² for melt-alloyed β brass within experimental error. As

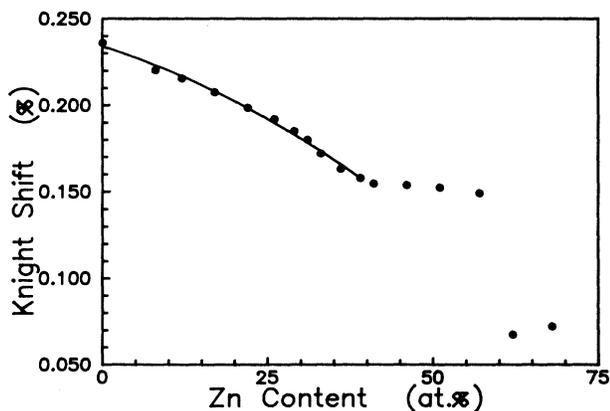


FIG. 2. The variation of the ^{63}Cu Knight shift for the alloyed Cu-Zn system, after milling of 12 h with zinc content.

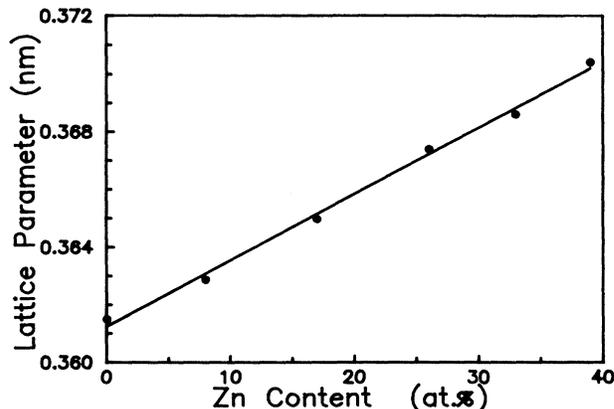


FIG. 3. The changes in the lattice parameter of the fcc phase vs the corresponding Zn content.

shown in Fig. 2, by increasing x from 40 to 57 at. %, the position of the ^{63}Cu resonance only slightly shifts from 0.155% to 0.149%. This resembles the results of West that the ^{63}Cu resonance frequency in β brass appears to be independent of composition, associating a fact that in those samples most of the Cu atoms are surrounded by a shell of approximate eight Zn atoms. In the fcc α phase, the decrease of K with the increase of the Zn content (x) can be fitted, as drawn in Fig. 2, with a solid line by

$$K = 0.2349 - 1.185 \times 10^{-3}x - 1.971 \times 10^{-5}x^2 \quad (1)$$

for $x < 39$, while the experimental value of the shift for the sample with maximum solubility of 39 at. % Zn is 0.159%, approaching that of the β phase. This behavior correlates with the structural character that the average number of Zn surrounding the ^{63}Cu nuclei is increased with x . It is easy to obtain that in the fcc solid solution of Zn in Cu there exists a relationship between x and N , the most probable nearby number of Zn atoms among the 12 sites of the first nearest neighbor around the Cu atom,

$$N = 12x / (100 - x) . \quad (2)$$

For small x , N is proportional to x , and for $x = 39$, N is closest to 8. Using Eq. (2) to obtain N from x , the

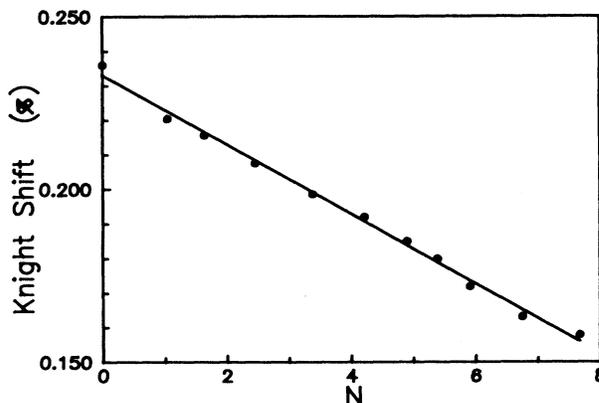


FIG. 4. The linear decrease of the ^{63}Cu Knight shift for alloyed fcc phase against N , the most probable nearby number of Zn atoms among the 12 sites of the first nearest neighbor around Cu atom.

changes of K against N are plotted in Fig. 4. It is clearly seen that in the fcc phase K decreases linearly with increasing N ,

$$K = 0.2331 - 0.01005N. \quad (3)$$

This means that the difference of the ^{63}Cu Knight shift in the alloy from that in pure copper is proportional to the number of first nearest neighbors which are Zn. As a counterpart, we have measured the value of K in α brass of $\text{Cu}_{65}\text{Zn}_{35}$ formed by melting as 0.1732%, close to the value of the MA sample. The results mentioned above indicate that the mechanically alloyed Cu-Zn system is very analogous to the melt-alloyed brass not only with the same crystallographic structure but also with similar electron distribution and atom configuration or CSRO.

The Knight shift of a probe nucleus in a metal is mainly determined by the electron density and wave functions in the metal. In its simplest form, it may be written as

$$K = (8\pi/3)\chi_p \langle |\psi_s(0)|^2 \rangle_{\text{FS}}, \quad (4)$$

where χ_p is the Pauli electron-spin susceptibility per atom, and $\langle |\psi_s(0)|^2 \rangle_{\text{FS}}$ is the square of the s -wave function at the nucleus averaged over those electron states at Fermi surface (FS).^{5,6} With respect to heavily deformed pure copper in which the peak position only slightly shifts down ($\Delta K \leq 0.004\%$) though the linewidth increases over 80.8 kHz due to a quadrupole broadening effect associated with the severe lattice distortion by ball milling,⁷ the ^{63}Cu Knight shift in the alloyed Cu-Zn system shows a significant decrease with Zn content increase (Fig. 2). This denotes a reduction of s -like electron density. Adlassnig *et al.*¹⁵ found, using the ^{67}Zn Mössbauer spectra, that in melt-alloyed Cu-Zn brasses the s -electron density around Zn atoms also reduces as the Zn content increases, which means a transfer of electron charge from the Zn atom to the Cu atom. Similar results would be obtained in MA samples since, as pointed out before, both samples prepared by melting or by MA have analogical CSRO. Hence, the wave functions around the Cu atoms are likely to assume a greater p character when Zn is added. This indicates that a strong interaction among the valence electrons of Cu and Zn has taken place, which causes the changes in wave functions probably through the admixture of a small amount of excited states into the ground state and/or the hybridization of s - and d -like electrons, and leads to the formation of new chemical bonds. Hence, a truly alloying reaction induced by MA has taken place.

The results for the α phase seem to conflict with that of BR.⁸ It can be explained in terms of quadrupole pertur-

bation effects. When Zn is alloyed with Cu, in addition to a change in the electron energy state, a redistribution of the electronic charge certainly takes place, both of which will affect the Knight shift. Concurrently, there would exist the interaction of ^{63}Cu nuclear electric quadrupole moments with electric-field gradients generated by the redistribution of electron charge due to Zn nearby. Even though the crystallographic structure of an alloy sample as determined by XRD has cubic symmetry, the environment of individual ^{63}Cu nuclei will not have this symmetry. The quadrupole interaction, which is constant for a given sample, perturbs the energy of the nuclear dipoles in an external magnetic field and shifts their transition energies appreciably.^{5,6} It could produce additive broadening so large that the signal becomes unobservable by a few scans. It is noted that the most limiting experimental aspect in 1953 was probably the 0.6-T field strength, making quadrupole effects on the central transition much larger than in 7-T and second-order quadrupole line shapes not symmetric. Perhaps due to the limitation of experimental conditions at that time, as pointed out by BR,⁸ NMR is only seen from those ^{63}Cu nuclei that are not close to the Zn atom, which have surroundings essentially the same as in pure copper and thus no great change in K should be expected. The characteristic variations of the ^{63}Cu Knight shift sometimes are masked. However, as we have done both, the signal-to-noise ratio can be improved by a signal accumulation of 10 000 or more scans and the quadrupole broadening effects be relatively abated by increasing the nuclear Zeeman energy using higher external magnetic field of 7.05 T. Furthermore, a similar tendency in K was observed in liquid Cu-Zn alloys⁹ where the quadrupole interaction has to be averaged over the rapidly changing configurations and effectively canceled. Recently, the value of the ^{63}Cu Knight shift of 0.16% in the alloy (Cu 66.5 at. % Zn 20.2 at. % Al 13.3 at. %) was reported by Rubini *et al.*¹⁶ So our results seem to be more reliable and probably reveal the characteristic variation of the ^{63}Cu Knight shift in Cu-Zn alloys. On the other hand, the general behavior of the ^{63}Cu Knight shift found in the present experiments on the Cu-Zn system by MA bears a striking resemblance to the pattern of results earlier established in Drain's experiments¹⁰ on melt-formed Ag-Cd alloys. This indicates that in the two analogous alloy systems, though prepared by different methods, there does not exist any fundamental difference between the electronic structures. It further suggests that present results reveal the characteristic variation of the ^{63}Cu Knight shift in Cu-Zn alloys.

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