Nuclear Magnetic Resonance of Amorphous Alloys $Cu_x Zr_{100-x}$ $(40 \leqq x \leqq 60)$ *

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^{91}Zr- and ^{63}Cu-NMR measurements of the amorphous alloys Cu_xZr_{100-x} $(40 \leqq x \leqq 60)$ are reported. By comparison of the experimental quadrupole disturbed spectra with simulated spectra of the amorphous alloys a short range order can be deduced, which is similar to the local lattice symmetry of the corresponding crystalline compounds. Furthermore the Knight shift of both nuclei in the alloys could be determined.

1. Introduction

Nuclear magnetic resonance (NMR) is a powerful method to determine – through quadrupole interactions – the local lattice symmetry and – through hyperfine interactions – the local electronic structure.

As has been shown by NMR of amorphous $T_{80}M_{20}$-alloys (T: transition metal, M: metalloid) [1] the crystalline short range order around the M-atom is mainly preserved. The question arises whether this finding is a feature of amorphous T-T alloys, too.

To check this we undertook measurements on amorphous alloys Cu_xZr_{100-x} for the composition range $40 \leqq x \leqq 60$. Both nuclei are detectable by NMR and have a nuclear spin $I > 1/2$. We begin by reporting experimental details, then we describe the evaluation procedure for the quadrupole disturbed NMR spectra and finally we interpret the results.

2. Experimental

The measurements were performed with a pulsed NMR spectrometer (Bruker SXP 4-100) for field strengths up to 5.2 T. The details of the apparatus are given in [2]. Because in transition metal alloys the electric field gradients can be very large and consequently the NMR spectra very extended, we developed a computer based technique to record the NMR transition by spin echo profiles [3].

The spin echo signal which can be very short (Fig. 1) is fed to a computer (PDP 11/10) by means of a transient recorder (Datalab, 50 ns/point). The time signal is integrated numerically in the indicateed window (cf. Fig. 1), accumulated and normalized. Simultaneously the corresponding magnetic field is read in through a digital voltmeter (Systron Donner, 5 1/2 digits). The integrals are stored as a function of the field. Thus it it possible to registrate very broad and weak lines continuously by using an optimized integrating window [4]. Furtheron it is possible to repeat the experiment for improving the signal-to-noise-ratio and to apply various computer routines to the spectra.

Typical spectra obtained by this technique are shown in Figs. 2 and 3. Since no crystalline compounds were available for this study, we compared the spectra of the amorphous alloys with those of the (crystalline) pure metals. While the spectrum

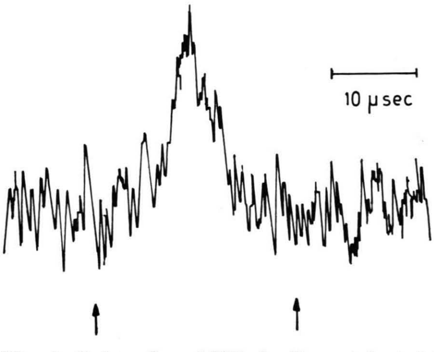

Fig. 1. Spin echo of ^{91}Zr in Zr metal at 4.2 K, one shot; the arrows indicate the time window for integration (see text).

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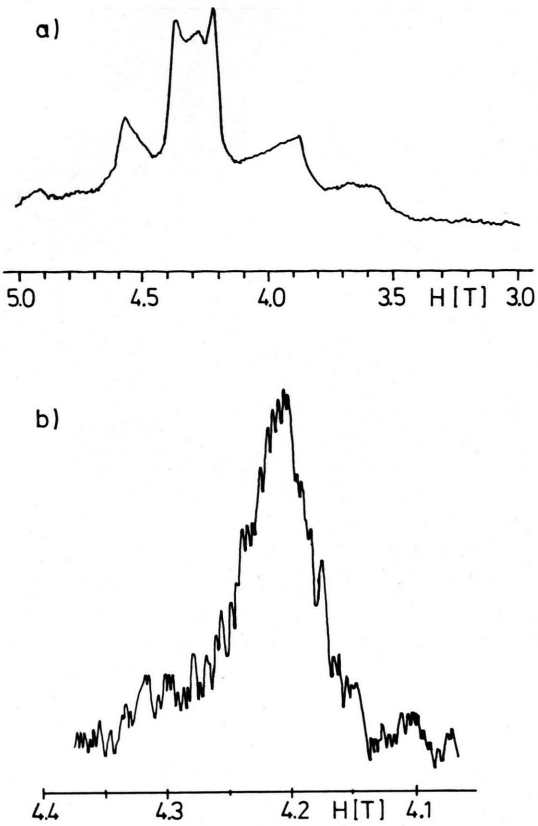

Fig. 2. Spin echo profiles of ^{91}Zr:
a) pure metal, $\nu_L = 17.014$ MHz;
b) amorpheus Cu$_{40}$Zr$_{60}$ alloy, $\nu_L = 16.694$ MHz.

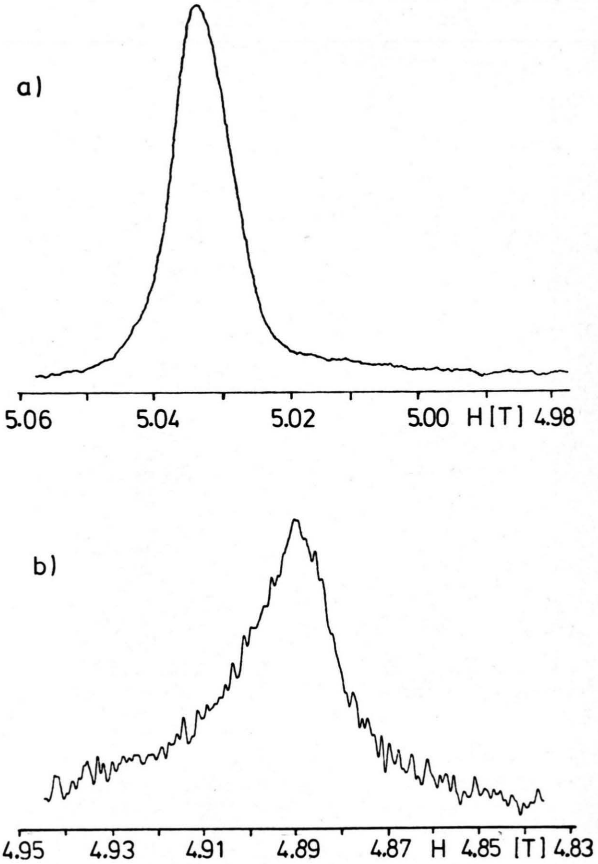

Fig. 3. Spin echo profiles of ^{63}Cu:
a) pure metal, $\nu_L = 56.796$ MHz;
b) amorphous Cu$_{60}$Zr$_{40}$ alloy, $\nu_L = 55.220$ MHz.

of Zr metal is representative for a hexagonal local symmetry leading to a pronounced structure, that of Cu metal is typical for a cubic local symmetry without any structure. The spectra of the amorphous alloys are characterized by a poorly developed structure. The latter ones represent the $(-1/2 \longleftrightarrow +1/2)$-transition of ^{63}Cu and ^{91}Zr, respectively. A detailed discussion is given in the next section.

3. Evaluation of the NMR Spectra

The interaction of the electric field gradient caused by the surrounding atoms with the quadrupole moment of the observed nucleus is described by $e^2 q Q/h$, the quadrupole coupling constant, and η, the asymmetry parameter. Both quantities are a measure for the deviation from cubic lattice symmetry [5].

In a powder the transition probability must be calculated at all possible orientations of the electric field gradient with respect to the applied magnetic field. Since an analytic expression cannot be given for powder spectra, $e^2 q Q/h$ and η are generally evaluated from the frequency dependence of prominent features of the lineshape (i. e. satellite singularities, splitting of the central line). The spectra of Zr metal can be evaluated conveniently in this way (Figure 4).

The line widths of the observed spectra of the amorphous alloys are inversely proportional to the frequency and therefore caused by quadrupole effects. Because of the poor resolution of the quadrupole structure simulated spectra were used to determine the characteristic parameters. We adopted the program of Taylor and Bray [6] which gives powder spectra including Knight shift and quadrupole effects up to the third order.

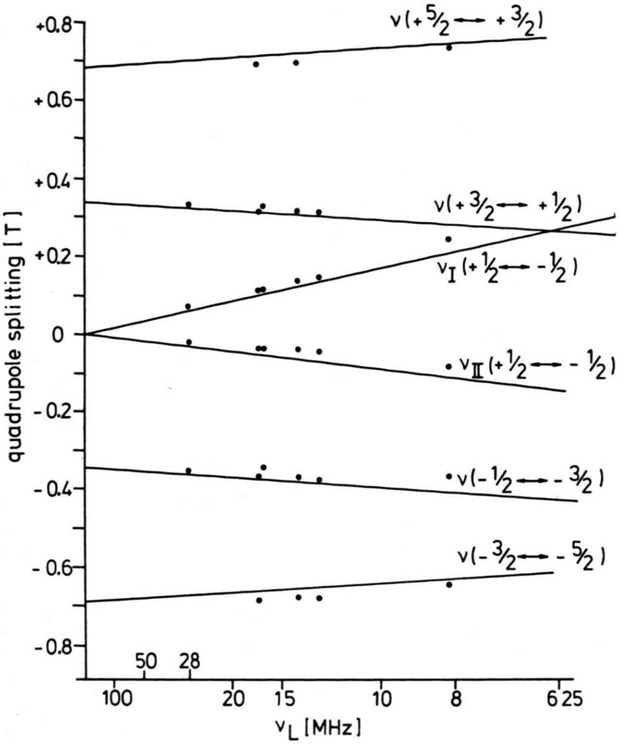

Fig. 4. Frequency dependence of the various transitions in pure zircon, relative to the Larmor frequency (field) of the "undisturbed" line. The points at 28 MHz are due to Hioki [13].

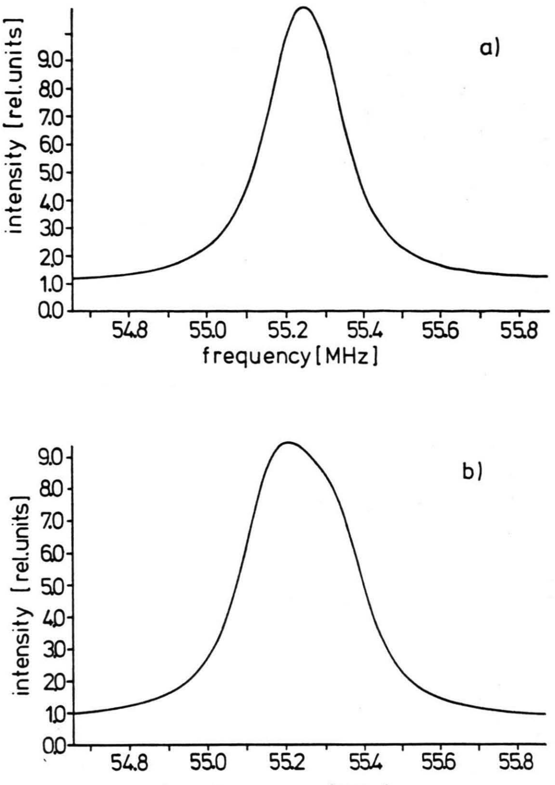

Fig. 5. Simulated spectra of ^{63}Cu for axial symmetry ($\eta = 0$) a) $|e^2 q Q/h| = 7.5$ MHz; b) $|e^2 q Q/h| = 10$ MHz, with the distribution parameter $\sigma = 170$ kHz for both cases. Only the frequency range which corresponds to the measured field spectrum in Fig. 3b is shown.

For an amorphous alloy different local environments and thus a distribution of the quadrupole parameters are to be expected. To take this into account we introduced a symmetric broadening function, characterized by the parameter σ. Because of the large quadrupole interaction in the alloys only the isotropic part of the Knight shift could be determined. The simulated spectra are converted by a linear relation [7] to field spectra. At the frequencies used the neglect of higher order terms introduces only a small error.

The broad distribution of $e^2 q Q/h$ and η smears out most of the characteristic features which can be observed in the spectrum of a crystalline system. The simulated spectra of ^{63}Cu demonstrate that in the case of axial symmetry mean values of $|e^2 q Q/h| \leqq 7.5$ MHz give a symmetric spectrum (Fig. 5 a), whereas greater values produce a shoulder at higher frequencies (lower fields; Figure 5 b). In a strongly anaxial case a quadrupole coupling constant of 7.5 MHz introduces already an asymmetric line (Fig. 6 a), for greater values a shoulder at lower frequencies (higher fields, Fig. 6 b) appears The ^{91}Zr spectra can be evaluated analogously.

4. Discussion

a) Short Range Order

From the comparison between the experimental and the simulated spectra of amorphous CuZr alloys we deduce that a preferred short range order exists.

In $Cu_{60}Zr_{40}$ and $Cu_{50}Zr_{50}$ from the simulation results for both nuclei a strongly anaxial local symmetry, while for $Cu_{40}Zr_{60}$ we find a nearly axial symmetric nearest neighbour arrangement. The quadrupole coupling constants show only a weak concentration dependence. The results are summarized in Table 1.

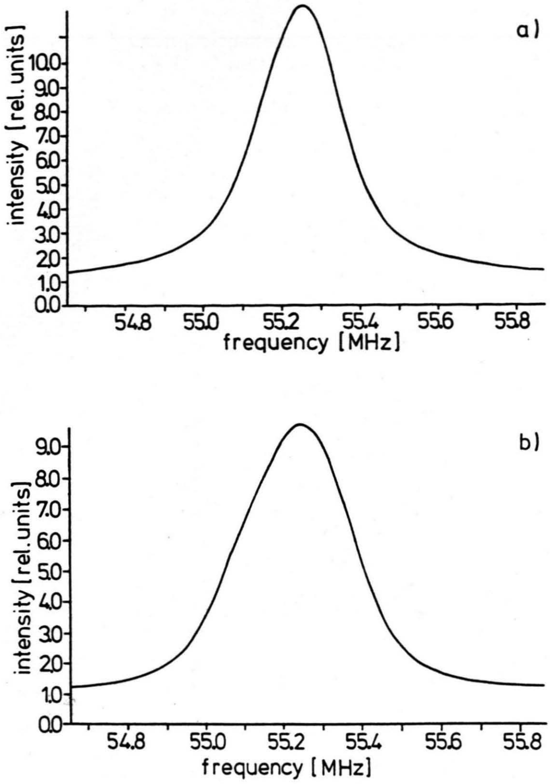

Fig. 6. Simulated spectra of ^{63}Cu for anaxial symmetry ($\eta = 0.7$): a) $\overline{|e^2 q Q/h|} = 7.5$ MHz, b) $\overline{|e^2 q Q/h|} = 10$ MHz; with the distribution parameter $\sigma = 170$ kHz for both cases.

The local symmetry seems to correlate with the structure of the stable crystalline compounds in this concentration range. For example, $Cu_{57}Zr_{43}$ has an orthorhombic structure [8], corresponding to an anaxial symmetry, whereas $Cu_{33.3}Zr_{66.7}$ has a tetragonal structure, corresponding to an axial symmetry.

b) Electronic Structure

The Knight shift values (K) deduced from the simulation procedure are given in Table 1 as well. The error limits are too large to give evidence for a pronounced variation of K_{Zr}. Optical measurements of the valence band [9] and band structure calculations [10] show that there are no important

Table 1. Quadrupole parameters and Knight shift values deduced from the simulation of the ^{63}Cu and ^{91}Zr spectra in the alloys Cu_xZr_{100-x} ($40 \leqq x \leqq 60$).

Alloy		$\underline{Cu}_{60}Zr_{40}$	$\underline{Cu}_{50}Zr_{50}$	$\underline{Cu}_{40}Zr_{60}$
$\overline{e^2 q Q/h}$	[MHz]	9.0 ± 1.0	9.0 ± 1.0	8.0 ± 1.0
$\overline{\eta}$		0.7 ± 0.2	0.6 ± 0.2	$\leqq 0.2$
σ	[kHz]	170	200	180
K_{Cu}	[%]	$+0.11$ (1)	$+0.07$ (1)	$+0.07$ (1)

Alloy		$Cu_{60}\underline{Zr}_{40}$	$Cu_{50}\underline{Zr}_{50}$	$Cu_{40}\underline{Zr}_{60}$
$\overline{e^2 q Q/h}$	[MHz]	10.0 ± 1.0	8.0 ± 1.0	8.0 ± 1.0
$\overline{\eta}$		0.7 ± 0.2	0.7 ± 0.2	$\leqq 0.2$
σ	[kHz]	260	260	200
K_{Zr}	[%]	$+0.30$ (5)	$+0.33$ (5)	$+0.30$ (5)

changes in the electronic structure of zircon in the alloy. This is at variance with measurements of Elschner et al. [11]. They find a strong increase of the orbital part. This discrepancy cannot be explained.

The copper Knight shift of the alloys is significantly smaller than that of pure copper. This indicates that the s-density of states is reduced in the alloys and that polarisation effects exist. The interpretation of K_{Cu} in alloys of platinum metals with Cu [12] suggests that a negative contribution to K_{Cu} arises due to the polarisation of the occupied s-bands. In our case the negative contribution grows with increasing zircon content and therefore is in accordance with the decreasing tendency of K_{Cu} as a function of composition. Because we have not yet measured the susceptibilities and the spin lattice relaxation times of the alloys we did not attempt to partition the Knight shift values.

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[1] P. Panissod, D. Aliaga Guerra, A. Amamou, J. Durand, W. L. Johnson, W. L. Carter, and S. J. Poon, Phys. Rev. Letters **44**, 1465 (1980).
[2] H. Herberg and J. Voitländer, Phys. Rev. **B 22**, 5043 (1980).
[3] W. G. Clark, Rev. Sci. Instrum. **35**, 316 (1964).
[4] W. Socher, J. Abart, and J. Voitländer, to be published.
[5] M. H. Cohen and F. Reif, Sol. State Physics **5**, 321 (1957).
[6] P. C. Taylor and P. J. Bray, J. Magn. Reson. **2**, 305 (1970); B. J. Bray, Priv. Comm. (1979).

[7] R. B. Creel and R. G. Barnes, J. Chem. Phys. **56**, 1549 (1972).
[8] L. Bsenko, J. Less. Common Metals **40**, 365 (1975).
[9] P. Oelhafen et al., Phys. Rev. Letters **43**, 1134 (1979).
[10] J. Kübler et al., Phys. Rev. **B 23**, 5176 (1981).
[11] H.-J. Eifert, B. Elschner, and K. H. J. Buschow, Priv. Comm. and Phys. Rev. B, in press.
[12] L. H. Bennett, E. Watson, and G. C. Carter, J. Res. NBS **74 A**, 569 (1970).
[13] T. Hioki, M. Kontani, and Y. Masuda, J. Phys. Soc. Japan **39**, 958 (1975).