Lattice instabilities during martensitic transformation in Cu-Zn-Al alloys by nuclear magnetic resonance

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Abstract

^{27}Al and ^{63}Cu measurements above, during and below the martensitic phase transformation of a Cu-Zn-Al alloy have been carried out. The temperature dependence of the spin-lattice relaxation rate and of the Knight shift for ^{27}Al is reported and discussed. The former prove the presence of lattice instabilities in a temperature region of about 10 K above and below the transformation temperatures, the latter an enhancement of the electronic density at the Al site in the martensite. NMR lineshape for ^{27}Al in austenitic and martensitic phase and for ^{63}Cu in austenitic phase are also reported and preliminary discussed.

Introduction

The martensitic transformations is often accompanied by anomalies of various physical parameters of the material. Those anomalies, as detected by electron diffraction, acoustic emission, internal friction and other methods of investigation [1,2] are observed in different thermoelastic alloys, like Ni-Ti or Cu-base alloys and seem to be present in a temperature range of about 30 K above the conventional transition point (M_s). The distances between the atoms and the symmetry of the environment at each crystallographic site are different in the austenite and martensite phases and lattice instabilities are present in the critical region. A powerful method to study local static and dynamic properties of the crystal, is the measurement of the nuclear magnetic resonance (NMR) parameters of a nucleus, used as a microscopic probe, reflecting the evolution of a critical effect [3].

The results of our first NMR work at moderate magnetic field ($H_o \cong 2$ T) on two Cu-base alloys have been published recently [4]. Here we report essentially on the high field ($H_o \equiv 7$ T) ^{27}Al and ^{63}Cu NMR measurements in a Cu-Zn-Al alloy.

The reason for the choice of a stronger field lies first in the improved sensitivity that one can reach, since NMR signal to noise ratio for a given nucleus has a $H_o^{3/2}$ (or $\nu_L^{3/2}$, where ν_L is the Larmor frequency of the nucleus) dependence, while the "skin depth" (i.e. the radio-frequency penetration) in a metallic sample is proportional only to $\nu_L^{-1/2}$. On the other hand the homogeneity of the high magnetic field, produced by superconducting solenoids is larger (by a factor 10^2 to 10^3) compared to that of classical magnets.

Therefore high field measurements have allowed us to perform more accurate studies for instance of the NMR line shape and the "Knight shift" [4,5].

Experimental

The polycrystalline samples of the alloy used for this study (composition (at %) $Cu_{67.6} - Zn_{17.4} - Al_{15}$ prepared from 3 N purity materials), were small pieces (0.5 mm^3) of metal of total volumes of about 1 cm^3, heat treated to decrease the vacancy concentration and then immersed in paraffin or in powdered quartz to avoid metal contact. The critical temperatures (M_S = 268 K, M_F = 258 K, A_S = 265.5 K, A_F = 277.5 K) were determined by DSC in a Perkin-Elmer calorimeter (Accuracy : $\Delta T \cong \pm 0.5$ K). The NMR measurements were carried out mainly in an Oxford superconducting magnet using a modified pulse Bruker SXP-100 spectrometer (Accuracy : $\Delta\nu_L \cong \pm 0.5$ kHz; $\Delta T_1^{-1} \cong 10$ %) The exact value of the external magnetic field (H_o = 6.987 T; homogeneity : $\Delta H/H_o \cong 10^{-7}$) have been determined by measuring the ^{27}Al Larmor frequency (ν_r) in a diamagnetic aqueous solution of the $AlCl_3$ salt. This value have also been used as reference for the "Knight shift" calculation. The temperature of the sample was stabilized better than 0.2 K using a "home-built" liquid N_2 cryostat.

Results and discussion

a. ^{27}Al-NMR spectra

Examples of the ^{27}Al-NMR recorded absorption spectra are shown in figure 1. In both (austenite and martensite) phases the spectrum

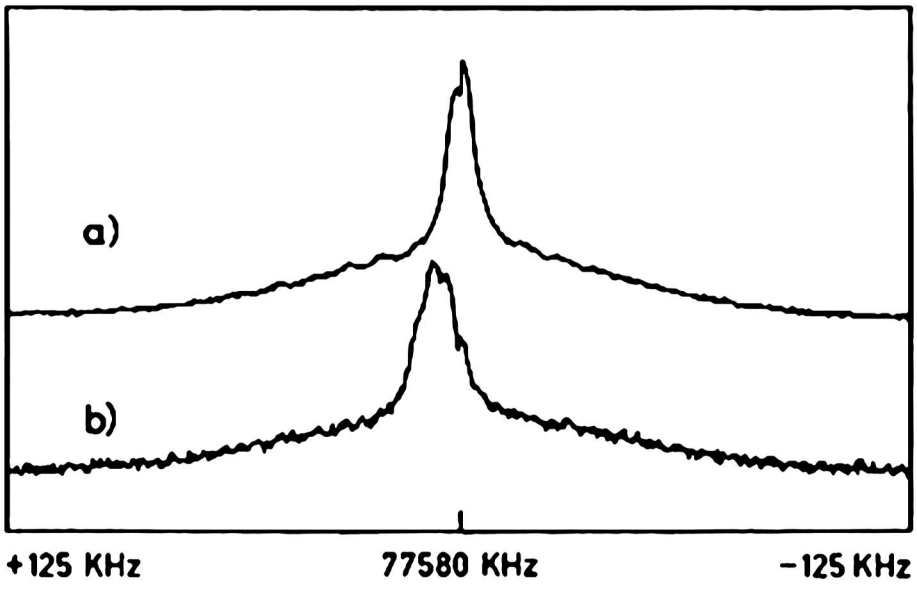

Fig. 1: ^{27}Al NMR spectra for $H_o \cong 7$ T at : (a) T = 291 K (b) T = 258 K. The frequency of the center of gravity of the line in the martensitic phase (T = 258 K) is about 5 kHz higher of the frequency in the austenitic phase.

consists of a rather narrow ($\Delta\nu_L \cong 20$ kHz) central transition and a broad line corresponding to transitions spread out over ± 100 kHz around the central line frequency. Above M_S, the central line has a doublet structure which seems to become a triplet one, below M_F. The doublet and triplet separation is of the order of 4 kHz. This line shape suggest two or three different sites for the ^{27}Al nucleus with different amounts of dipolar magnetic or quadrupolar electric interactions, or an anisotropic Knight shift [6]. Magnetic splittings are proportional to the applied magnetic field, first order quadrupole splittings are field independent and second order quadrupole splittings are inversely proportional to the external magnetic field. In order to determine the origin of the observed structures, some measurements at low field ($H_o \cong 1.8$ T) have been performed. In that case no structure is observable in the central line, whereas the shape of the broad line around the central frequency is identical to that observed at high field. These results support strongly the assumption that the origin of the central line splitting is magnetic and the broad line is due to a first order quadrupole satellites distribution, which indicate a non cubic local symmetry even in austenitic phase.

b. ^{63}Cu-NMR spectra

A spectrum of the ^{63}Cu-NMR absorption in the austenite phase is displayed in figure 2. Preliminary measurements below M_F have shown

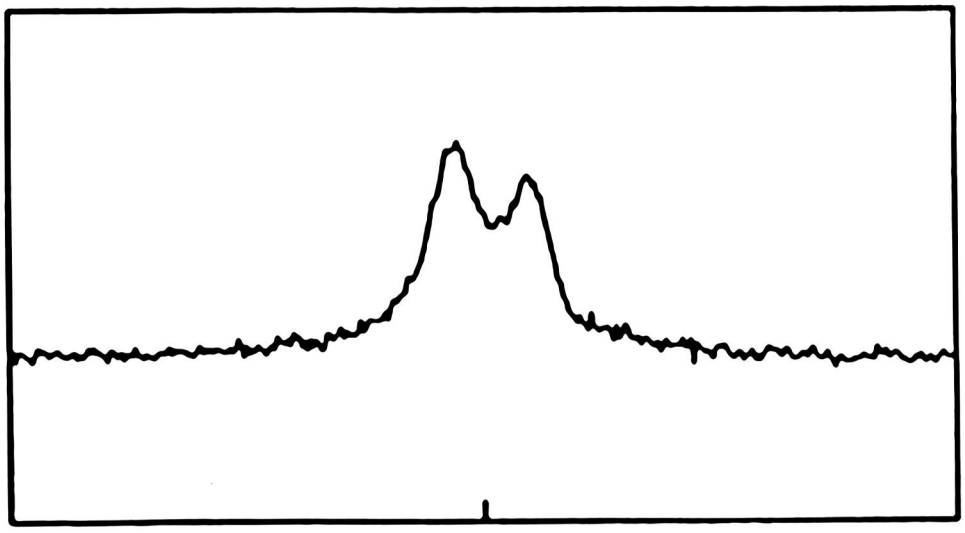

Fig.2: ^{63}Cu NMR spectrum for $H_o \cong 7$ T at T = 293 K.

that the doublet structure (separation of about 31 kHz) observed at high temperature evolves progressively to a single rather broad line ($\Delta\nu \cong 60$ kHz). At low field ($H_o \cong 2.3$ T) the doublet separation becomes 10 kHz, corresponding to the value expected for a magnetic origin splitting.

c. Knight shift

The resonance frequency in metals (ν_m) is in most cases higher than that of the same isotope in an insulating material (ν_r) in the same

magnetic field. This difference named the "Knight shift" can be expressed as :

$$\frac{n_m - n_r}{n_r} \cdot 100 = \mathcal{K} \text{ (in \%)} \qquad (1)$$

and is caused by the paramagnetic susceptibility of the conduction electrons at the Fermi surface [6]. The temperature dependence of $\mathcal{K}$ for the ^{27}Al nucleus is shown in figure 3. The mean value of $\mathcal{K}$ in

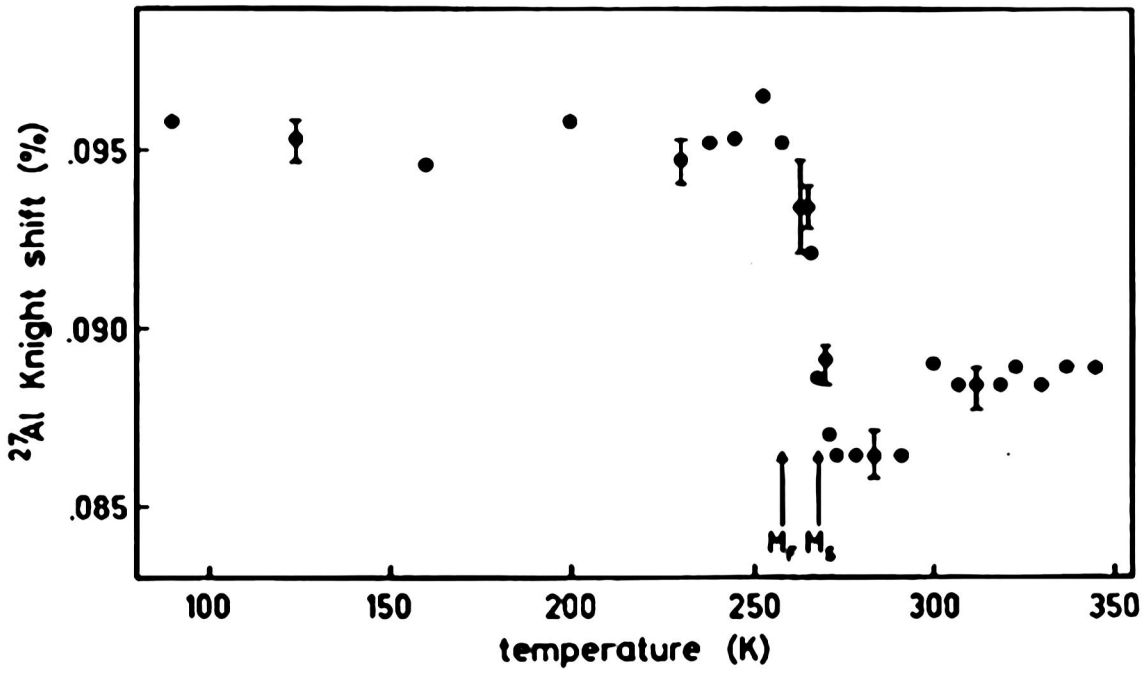

Fig. 3: Temperature dependence of the ^{27}Al Knight shift.

the austenite phase is about 0.088 %. A jump of this value to @ 0.096 % is observed at the transition region. This results, prove that the local electronic density around the ^{27}Al nuclei at the Fermi surface is higher in the martensitic than in the austenitic phase.

d. ^{27}Al-NMR relaxation

Nuclear relaxation is the process which causes a spin system to attain its equilibrium distribution after a perturbation, for example following a p/2 rf pulse. The characteristic time constants for the spin-spin equilibrium and the spin-lattice thermal equilibrium are defined as T_2 and T_1 respectively. For simple metals, where both the Knight shift and the nuclear spin-lattice relaxation are dominated by the contact term of the nuclear-electronic hyperfine interaction, Korringa derived the relation [6,7] :

$$\mathcal{K}^2 \, T_1 \, T = S \, , \qquad (2)$$

with : $S = (g_e/g_n)^2 \, (h/8 \, p^2 \, k_B)$

where g_e and g_n are the electronic and nuclear gyromagnetic ratios and k_B the Boltzmann constant. The "Korringa ratio" $\mathcal{K}^2 \, T_1 \, T/S$ is

ideally equal to unity, but deviations arising from many sources can be observed in alloys and even in pure metals.

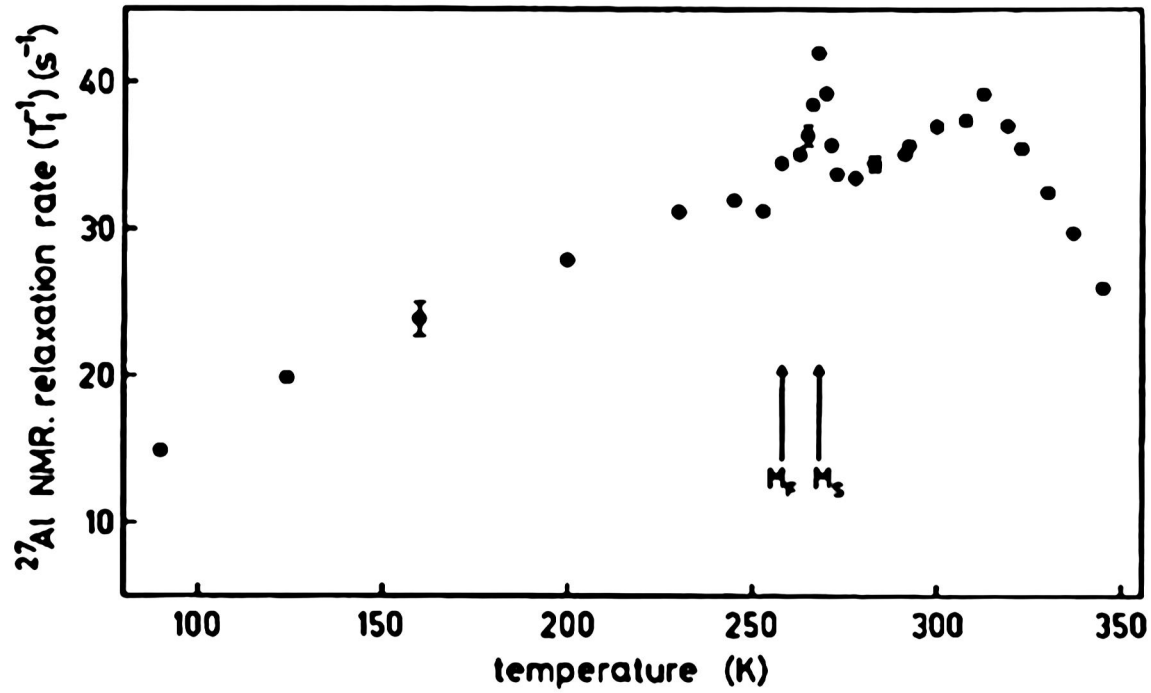

Fig. 4: Temperature dependence of the ^{27}Al spin-lattice relaxation rate ($H_0 \cong 7$ T)

In figure 4, we have presented the evolution of the ^{27}Al NMR relaxation rate T_1^{-1} as a function of the temperature. A maximum is observed in the transformation region and a second maximum around 312 K. At low temperatures, a deviation from the ideal Korringa relation seems to be present. The first maximum can be attributed to the onset of critical lattice fluctuations and the second to the "classical" ($\omega_L \tau_c \sim 1$) condition, where τ_c is the correlation time corresponding to thermally activated motions in the lattice [3,4]. Complementary measurements are in progress for a quantitative analysis of the T_1^{-1} data.

Conclusion

The ^{27}Al and ^{63}Cu NMR line shapes, points towards (at least for the copper atoms) the existence of two magnetically inequivalent sites in the crystal. In addition, the local environment in the Al site seems to have a lower than cubic symmetry, even in the austenite phase. An enhancement of the electronic density in the Al sites occurs in the martensite phase. Lattice instabilities are present in a temperature region of about 10 K above and below the transformation temperature.

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