

## Martensitic transformation in Ag-Cd and Cu-Zn alloys studied by nuclear magnetic resonance

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$^{113}\text{Cd}$ ,  $^{109}\text{Ag}$ , and  $^{63}\text{Cu}$  nuclear-magnetic-resonance line-shape and Knight-shift measurements are reported for  $\text{Ag}_{53.5}\text{Cd}_{46.5}$  and  $\text{Cu}_{61}\text{Zn}_{39}$  over a temperature interval covering the martensitic phase transformation (MPT) displayed by these alloys. The changes observed in the line shape and width are explained in terms of the changes in atomic coordination and crystal symmetry occurring at the MPT. A small but non-negligible temperature dependence of the Knight shift is observed in the austenitic phase with small discontinuous changes at the transformation for all the nuclei investigated. The difference of resonance frequency of  $^{113}\text{Cd}$  in the two phases has been utilized to obtain the curve of the percentage of martensite in the Ag-Cd alloy as a function of temperature during the thermoelastic transformation. It is shown that our growth curve reveals details which cannot be seen by dynamical methods such as differential scanning calorimetry.

### I. INTRODUCTION

Several noble-metal-based and Ni-based alloys near the equiatomic concentration display a diffusionless structural phase transformation from a high-temperature bcc structure (austenite) to a compact structure (martensite). The transformation is first order, and belongs to the class of the martensitic phase transformations (MPT's).<sup>1</sup> It takes place by nucleation of martensitic regions at the temperature  $M_S$  and proceeds by the growth of the martensite in the austenitic matrix by lowering the temperature down to  $M_F$ . In the temperature range between  $M_S$  and  $M_F$  the two phases coexist in thermoelastic equilibrium, and special mechanical effects like shape memory and superelasticity<sup>2</sup> are associated with the MPT.

The thermodynamic grounds of the MPT in this kind of alloy are nowadays known: the open bcc structure is favored at high temperature by the high vibrational entropy vis-à-vis the compact structure which is characterized by a higher cohesive energy.<sup>3,4</sup> However, the understanding of the microscopic mechanisms that make the transformation possible is still incomplete: open questions concern the nature of the nucleation sites, the presence of precursors, and the role of the observed partial softening of phonons and elastic constants.<sup>5</sup>

Nuclear magnetic resonance (NMR) was recently applied as a microscopic investigation technique to the study of the MPT in shape memory alloys. Interesting results were obtained concerning the local crystallographic and electronic structure in a Cu-Zn-Al alloy<sup>6</sup> and Ni-Al alloys.<sup>7</sup> The main results arise from the analysis of the Knight shift

$$K = \frac{\nu - \nu_0}{\nu_0} = \frac{8\pi}{3} \langle |\psi(r_n)|^2 \rangle_{E_F} \chi, \quad (1)$$

which relates the observed resonance frequency  $\nu$  in the metal to features of the electronic structure. In Eq. (1)  $\nu_0$  is the resonance frequency of the same nucleus in a diamagnetic reference compound,  $\langle |\psi(r_n)|^2 \rangle_{E_F}$  is the square of the electronic wave function at the nuclear site, averaged on the Fermi surface, and  $\chi$  is the electronic spin susceptibility, proportional to the electronic density of states at the Fermi energy. Changes of the Knight shift at the MPT were observed for  $^{27}\text{Al}$  and  $^{63}\text{Cu}$  resonance in two Cu-Zn-Al alloys<sup>6,8</sup> and for the  $^{27}\text{Al}$  resonance in Ni-Al alloys of different composition.<sup>7</sup> In the latter case, the analysis of the Knight-shift results together with those of low-temperature calorimetry and magnetic-susceptibility measurements in Ni-Al suggests that the observed changes are mainly due to symmetry changes of the wave function at the Fermi energy, without major changes in the total density of states, that would be reflected in  $\chi$  and in the specific heat. The difference of resonance frequency in the two phases results in two NMR signals whose relative intensity yields the percentage of martensite present at any intermediate stage of the thermoelastic transformation. In Cu-Zn-Al an explosive nucleation of fully transformed martensite was observed, while in Ni-Al alloys evidence was found for nucleation of a partially transformed phase, with a structure intermediate between the austenite and the martensite. The growth of this phase was accompanied by a progressive distortion of the lattice toward the martensite structure.

Other interesting information arises from the analysis of the line shape for nuclei with strong quadrupole interaction, like  $^{63}\text{Cu}$ . In Cu-Zn-Al the combined analysis of Knight shift and line shape of  $^{27}\text{Al}$  and  $^{63}\text{Cu}$  resonances gave information about the order of the ternary alloy.<sup>6</sup>

In all the Cu-Zn-Al alloys we considered, the transformation is accompanied by an anomalous enhancement of the  $^{63}\text{Cu}$  and  $^{27}\text{Al}$  spin-lattice relaxation rate.<sup>6,8</sup> In met-

als the main relaxation mechanism is driven by the interaction between nuclear spins and the conduction electrons at the Fermi energy, and the spin-lattice relaxation rate is related to the Knight shift  $K$  by the Korringa relation,

$$T_1^{-1} = \frac{4\pi k_B}{\hbar} \left( \frac{\gamma_N}{\gamma_e} \right)^2 k(\alpha) K^2 T, \quad (2)$$

where  $\gamma_N$  and  $\gamma_e$  are the nuclear and electronic gyromagnetic ratios and  $k(\alpha)$  is an enhancement factor which takes into account the exchange and correlation effects in the conduction-electron Fermi gas as a function of the Stoner parameter  $\alpha$ . The observed effect in Cu-Zn-Al was interpreted as due to local electronic fluctuations related to atomic motions at the interfaces between the coexisting phases.<sup>6</sup> No enhancement of the <sup>27</sup>Al relaxation rate was observed in Ni-Al alloys.

In the present study we extend our investigation to other noble-metal alloys by performing <sup>63</sup>Cu, <sup>113</sup>Cd, and <sup>109</sup>Ag NMR in Cu<sub>61</sub>Zn<sub>39</sub> and Ag<sub>53.5</sub>Cd<sub>46.5</sub>. Since the application of NMR techniques to the study of the MPT is only at its birth, the observation of patterns of similarities and differences for the same nuclei in different alloys and for different nuclei in the same alloy is of paramount importance.

The two systems are chemically similar, differing only in the position of the constituent elements in the row of the periodic table. In the high-temperature phase both alloys are ordered in a CsCl structure: one of the cubic sublattices is completely occupied by the noble-metal atoms, the second is occupied mainly by the divalent atoms, with the excess noble metal randomly distributed as antisite defects. The low-temperature phase is a stacking of compact planes with periodicity 2 (a deformed hcp structure) in Ag-Cd,<sup>9</sup> and 9 in Cu-Zn.<sup>10</sup> The transformation take place without diffusion, and the main effect on the local geometry is the change of coordination of each atom: in the bcc-based structure each atom has eight nearest neighbors (NN), in the compact structure 12, and at the MPT four atoms of the CsCl second-neighbor shell move to a distance similar to that of the NN. These changes of coordination and symmetry are clearly detectable by NMR.

The interest of a parallel investigation of Cu-Zn and Ag-Cd alloys is due to the different characteristic of the resonant nuclei. In Cu-Zn the NMR of the two Cu isotopes can be studied, whereby the isotopes have similar magnetic and quadrupole moments with <sup>63</sup>Cu yielding the strongest signal. <sup>63</sup>Cu is very sensitive to the presence of an electric field gradient (efg) and therefore to the local symmetry at the nuclear site. As a consequence the resonance lines are often broad due to a distribution of second-order quadrupole effects related to local disorder.

In Ag-Cd both <sup>113</sup>Cd and <sup>109</sup>Ag have spin  $I = 1/2$  and are insensitive to quadrupole interactions. Both have a sizable Knight shift, and the change of resonance frequency at the MPT is large and allows a good resolution of the two signals originating from the coexisting phases. This circumstance has been utilized for <sup>113</sup>Cd to construct with high precision the transformation curve of

martensite vs  $T$  and to get information about the behavior of the transformation. <sup>109</sup>Ag has a very weak signal which makes difficult a detailed study of the line shape in the transformation region and of the relaxation. The results about the Knight shift in the two phases are very important because they are complementary to those of <sup>63</sup>Cu in Cu-Zn affected by quadrupole interactions.

## II. SAMPLES AND EXPERIMENTAL METHODS

The Ag-Cd alloy was prepared by melting high-purity materials in argon atmosphere at 1273 K with vigorous stirring. To prevent segregation, the liquid alloy was quickly cooled to room temperature by dropping it in water. The oxide surface was mechanically removed and the ingot was annealed at 950 K in vacuum and then quenched into iced water. The Cu-Zn sample was obtained from a single crystal grown at the Laboratorium für Neutronenstreuung of the P. Scherrer Institute (Villingen, Switzerland).<sup>11</sup> The NMR sample was in both cases an assembly of small cubes embedded in powdered quartz (0.3 mm per side, obtained from the ingot using a multiple-wire saw).

The transformation temperatures determined by differential scanning calorimetry (DSC) are  $M_S = 144$  K,  $M_F \simeq 120$  K for Ag-Cd and  $M_S = 178$  K,  $M_F \simeq 120$  K for Cu-Zn. Both alloys were cycled 20 times through the transformation in order to stabilize the transformation path before the NMR measurement. All the NMR measurements were performed at equilibrium at a fixed temperature monitored during the measurement by a thermocouple embedded in the sample.

Standard techniques of pulse NMR were used in the absorption-spectra and relaxation-time measurements. The absorption spectra were obtained by Fourier transform of half of the echo (<sup>63</sup>Cu and <sup>113</sup>Cd) or of the free-induction decay (<sup>109</sup>Ag).

The exact value of the field for the Knight-shift measurements was determined by means of the resonance frequency of <sup>27</sup>Al in an AlCl<sub>3</sub> aqueous solution for the <sup>63</sup>Cu measurements, and of <sup>113</sup>Cd in CdCl<sub>2</sub> aqueous solution for the <sup>113</sup>Cd measurements. In the case of the <sup>109</sup>Ag measurements, due to the weakness of the NMR signal, the reference was determined by measuring the <sup>109</sup>Ag resonance frequency at  $T = 300$  K in a sample of pure silver particles (35  $\mu$ m) mixed with TiO<sub>2</sub> powders, and using for the <sup>109</sup>Ag in silver metal the Knight shift reported by Sahn and Schwenk,<sup>12</sup> i.e.,  $K(^{109}\text{Ag}, 300 \text{ K}) = 0.521\%$ , referred to Ag<sup>+</sup> ions in water at infinite dilution.

## III. RESULTS

The <sup>113</sup>Cd absorption spectra recorded at three temperatures in the Ag-Cd alloy are presented in Fig. 1. At high temperature the <sup>113</sup>Cd spectrum is a single narrow Gaussian line [Fig. 1(a)]. The linewidth (5 kHz) is nearly temperature independent from room temperature down to 143 K. In the same temperature region the Knight shift

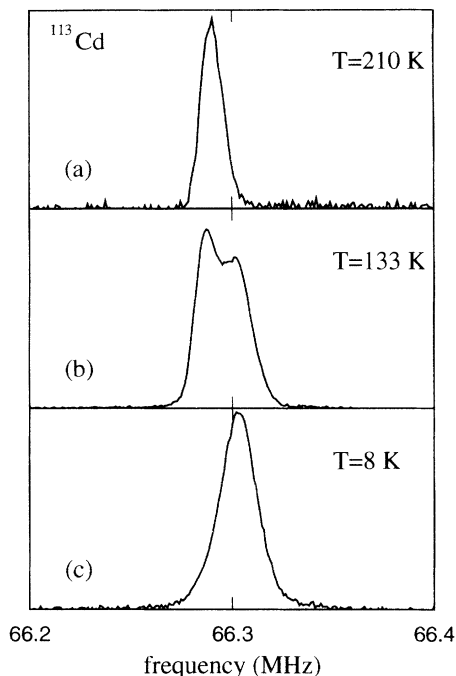


FIG. 1.  $^{113}\text{Cd}$  NMR spectra in the Ag-Cd alloy as a function of temperature at  $H_0 = 7$  T. (a)  $T > M_S$ , (b)  $M_S > T > M_F$ , (c)  $T < M_F$ .

displays an almost linear temperature dependence (see Fig. 2). At the onset of the MPT the  $^{113}\text{Cd}$  spectrum splits into two lines [Fig. 1(b)]. The new, high-frequency line corresponds to the martensitic phase and the splitting is due to the coexistence of the two phases. At the lowest temperature only a symmetric line (of about 10 kHz width) is present, representative of the martensite [Fig. 1(c)]. The Knight shift of the martensitic phase, shown in Fig. 2, is temperature independent.

The  $^{109}\text{Ag}$  spectrum is a single line, with a Gaussian shape, and a width of about 1 kHz in the high-temperature phase and 2 kHz in the low-temperature

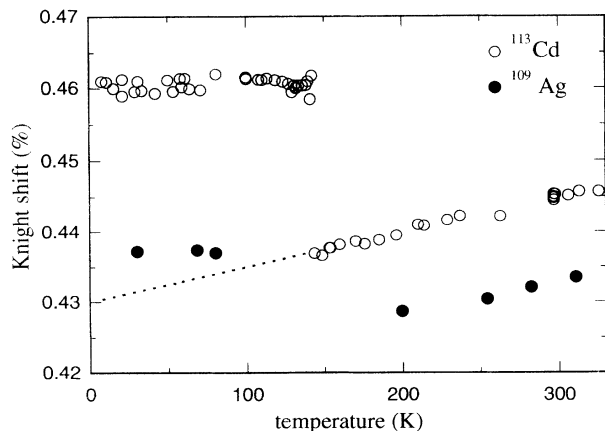


FIG. 2.  $^{113}\text{Cd}$  Knight shift as a function of temperature. Some measurements of the  $^{109}\text{Ag}$  Knight shift in the two phases are also reported.

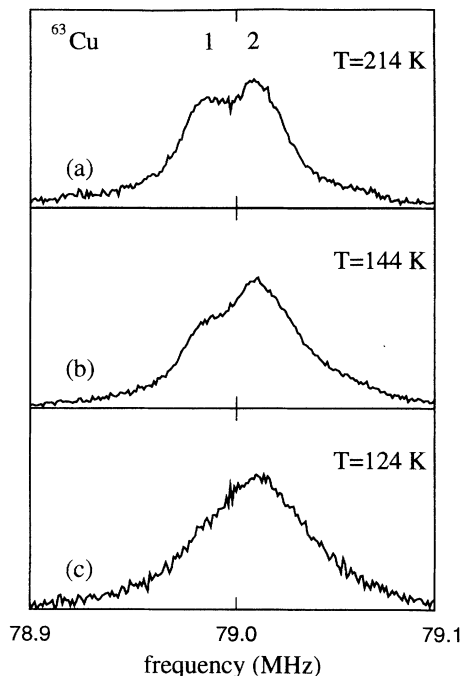


FIG. 3.  $^{63}\text{Cu}$  NMR spectra in the Cu-Zn alloy as a function of temperature at  $H_0 = 7$  T. (a)  $T > M_S$ , (b)  $M_S > T > M_F$ , (c)  $T < M_F$ . The two lines present above  $M_S$  (a) will be labeled line 1 (low frequency) and line 2 (high frequency), respectively.

phase. The Knight shift, reported in Fig. 2, displays a linear temperature dependence in the austenite, and is constant in the martensite.

The  $^{63}\text{Cu}$  absorption spectra in Cu-Zn at three different temperatures are shown in Fig. 3. At high temperature the spectrum is composed of a doublet whose separation is linearly field dependent, indicating the presence of two Cu sites with different Knight shifts. At the onset of the transformation the high-frequency line progressively disappears and in the martensitic phase a single asymmetric line broadened by quadrupole interaction is left.

The  $^{63}\text{Cu}$  and  $^{113}\text{Cd}$  spin-lattice relaxation rates follow a Korringa-like behavior [Eq. (2)] in the two phases with a change of slope at the transformation consistent with the change of Knight shift between the austenite and the martensite. No anomalous enhancement of the relaxation rate can be observed in the neighborhood of the transformation.

#### IV. DISCUSSION

Let us begin the discussion by the analysis of the  $^{113}\text{Cd}$  results. The observed linewidth depends linearly on the applied magnetic field. In the austenite the homogeneous width obtained from the extrapolated value at zero field agrees well with the square root of the second moment of the line  $\sqrt{M_2} = 50$  Hz, computed according to the Van Vleck formula for spin-spin dipolar interaction.<sup>13</sup> The field-dependent inhomogeneous broadening should be as-

cribed to a distribution of Knight shifts, corresponding to 1.5% of the value for the center of the line, due to a distribution of second-neighbor configurations. In the low-temperature phase the broadening, always of magnetic origin, is more pronounced, due to the disorder at the NN distance associated with the distortion of the structure.

Let us consider now the dependence of the  $^{113}\text{Cd}$  and  $^{109}\text{Ag}$  Knight shifts on the temperature (Fig. 2). In Table I the values of the Knight shifts of the pure metals and of the alloys are summarized at  $T=300$  K together with their temperature dependence expressed by the value of  $\partial \ln K / \partial T$ .

The very strong temperature dependence of the  $^{113}\text{Cd}$  Knight shift in pure cadmium metal<sup>14</sup> has been interpreted in terms of lattice expansion and electron-phonon interactions<sup>15</sup> in the presence of a pseudogap at the Fermi surface.<sup>16</sup> On the other hand, the weak variation of the noble-metal Knight shift in the pure metals has been explained simply by the effect of lattice expansion on the  $s$ - $d$  hybridization.<sup>17,18</sup> The temperature dependence of the  $^{113}\text{Cd}$  and  $^{109}\text{Ag}$  Knight shifts in the Ag-Cd alloy is the same as that of  $^{63}\text{Cu}$  in the Cu-Zn alloy, and also of  $^{27}\text{Al}$  and  $^{63}\text{Cu}$  in the austenitic phase of Cu-Zn-Al (see Ref. 6).

The temperature dependence in the present alloys is larger than in the noble metals (see Table I) although of the same order of magnitude. This should indicate that, although the Fermi surface may be close to the Brillouin zone, no pseudogap effects of the type observed in Cd metal are present here.

In the compact low-temperature phase the  $^{109}\text{Ag}$ ,  $^{113}\text{Cd}$ , and  $^{63}\text{Cu}$  Knight shifts are constant and so are also those of  $^{27}\text{Al}$  and  $^{63}\text{Cu}$  in the martensitic phase of Cu-Zn-Al (see Ref. 6). This is probably due to a minor sensitivity of the electronic structure of the compact crystal to thermal expansion.

Let us turn now to the analysis of the  $^{63}\text{Cu}$  spectra and their relation with the local symmetry of the alloys. The  $^{63}\text{Cu}$  line shape and its temperature evolution in the Cu-Zn alloy are similar to those observed in the Cu-Zn-Al alloy studied in Ref. 6.

It is well known that in polycrystalline samples the quadrupole interaction can wipe out the resonance of all

the  $^{63}\text{Cu}$  nuclei but those in a local NN configuration, yielding a nearly zero efg.<sup>19</sup> In the case of the Cu-Zn-Al alloy<sup>6</sup> two kinds of Cu sites with nearly zero efg were found: Cu antisites having only Cu as NN's, and pure Cu sites with a particular mixed NN configuration giving a zero efg at the nuclear site. In the low-temperature (and low-symmetry) martensitic phase, only the first kind of Cu site contributes to the signal. A quantitative analysis of the  $^{27}\text{Al}$  and  $^{63}\text{Cu}$  Knight-shift results allowed us to attribute the high-frequency line (line 2) to the antisite Cu.<sup>6</sup>

The results obtained in the Cu-Zn alloy can be analyzed on the same basis. As in Cu-Zn-Al DO3 alloys, in the CsCl Cu-Zn alloy two kinds of Cu sites with nearly zero efg are present: antisite Cu having only Cu atoms as NN's (about 18% of the total number of Cu atoms for the 41 at. % Zn alloy), and a fraction of pure Cu sites (about 14.3% of the total number) having a mixed NN configuration. An inspection of the numerical values of the Knight shifts of the two  $^{63}\text{Cu}$  lines in the austenite ( $K_1$  and  $K_2$ ) and of the single line in the martensite ( $K_M$ ) for the two alloys gives the following ratios:  $(K_1/K_M)(\text{Cu-Zn})=0.83$ ,  $(K_2/K_M)(\text{Cu-Zn})=0.98$ ,  $(K_1/K_M)(\text{Cu-Zn-Al})=0.75$ , and  $(K_2/K_M)(\text{Cu-Zn-Al})=0.98$ .

Taking into account the above ratios, the estimated number of atoms on the two sites with zero efg, and the observed intensity of the absorption lines, we can infer that line 2 (see Fig. 3) corresponds to the antisite  $^{63}\text{Cu}$  nuclei, having a pure Cu NN environment. In the martensitic phase the line 1 (see Fig. 3) disappears because the lattice distortion introduces a large efg at all the pure Cu sites. The line 2 arising from antisite  $^{63}\text{Cu}$  nuclei is still detectable but is broadened by second-order quadrupole effects related to the distortion of the first-NN shell, described in the Introduction.

Indirect confirmation of this conclusion can be found in the analysis of the  $^{109}\text{Ag}$  Knight-shift data in the Ag-Cd alloy. As mentioned in the Introduction, silver in the Ag-Cd alloy is equivalent to copper in the Cu-Zn alloy and it occupies mainly one of the cubic sublattices of the CsCl structure, with only 2% of Ag being randomly located on the Cd sublattice. Since the  $^{109}\text{Ag}$  nucleus is insensitive to quadrupole interactions, all the  $^{109}\text{Ag}$  nuclei of the alloy contribute to the observed NMR signal, but due to the relative number of atoms on the two sublattices, the observed absorption line is essentially due to the  $^{109}\text{Ag}$  nuclei on the pure silver sublattice.  $^{109}\text{Ag}$  data therefore give information about the evolution of the electronic structure around nuclei on the pure noble-metal sublattice characterized by a disordered distribution of NN's, the site being inaccessible in the martensite in the case of Cu-Zn as argued above.

By calculating the ratio between the Knight shift in the austenitic phase near  $M_S$  and in the martensitic phase we find  $(K_A/K_M)(^{109}\text{Ag})=0.975$ , and  $(K_A/K_M)(^{113}\text{Cd})=0.945$ . These values are both close to the analogous ratios for the  $^{63}\text{Cu}$  line 2 in Cu-Zn and for  $^{27}\text{Al}$  and  $^{63}\text{Cu}$  in Cu-Zn-Al (0.98 and 0.93, respectively).<sup>6</sup>

We conclude that changes of similar size take place at the MPT in the local electronic structure in all the investigated noble-metal alloys. The size of the change is

TABLE I. Knight shift  $K$  and temperature dependence  $(\partial \ln K / \partial \ln T)_P$  in pure metals and alloys at 300 K.

Material	Nucleus	$K(300 \text{ K})$	$(\partial \ln K / \partial \ln T)_P$ ( $10^4 \text{ K}^{-1}$ )
Cd metal	$^{113}\text{Cd}$	0.414% <sup>a</sup>	7.5 <sup>a</sup>
Cu metal	$^{63}\text{Cu}$	0.239% <sup>b</sup>	0.4 <sup>b</sup>
Ag metal	$^{109}\text{Ag}$	0.521% <sup>c</sup>	0.4 <sup>c</sup>
Ag-Cd	$^{109}\text{Ag}$	0.432%	0.9
Austenite	$^{113}\text{Cd}$	0.445%	1.1
Cu-Zn	$^{63}\text{Cu}(1)$	0.194%	1.0
Austenite	$^{63}\text{Cu}(2)$	0.164%	1.2

<sup>a</sup>Reference 14.

<sup>b</sup>Reference 17.

<sup>c</sup>Reference 18.

similar at all the lattice sites.

In Ni-Al alloys, where no change of the magnetic susceptibility was found at the transition, the Knight-shift discontinuity at the MPT was ascribed to the change of symmetry of the conduction-electron wave function at the nuclear site. On the other hand, in the noble-metal alloys there is evidence for a small discontinuity in the magnetic susceptibility.<sup>20</sup> Furthermore, the Knight-shift jump has opposite sign than for Ni-Al, and is accompanied by a change in the Knight-shift temperature dependence. Thus in noble-metal alloys changes both in the density of states and in the symmetry of the electron wave function at the Fermi energy should be invoked.

Let us consider now the  $^{113}\text{Cd}$  spectra during the MPT. Below  $M_S$ , two resonance lines coexist centered at different frequencies and with a relative amplitude which is a function of temperature, the two signals belonging to the martensite and to the austenite respectively. A quantitative evaluation of the fraction of martensite present in thermoelastic equilibrium at each temperature can be obtained by the deconvolution of the absorption line in the two components, following the scheme discussed in Ref. 6.

The fit has been performed by assuming that, between  $M_S$  and  $M_F$ , the line of the austenite has a frequency which extrapolates the linear temperature dependence observed above  $M_S$ , and constant width given by the value measured at  $M_S$ . The frequency of the martensite is found to be constant, the Knight-shift values reported in Fig. 2. The constant value obtained for the Knight shift of the martensite is certainly not an artifact due to the fit, being the same near  $M_S$  (were the assumption is certainly valid) and at very low temperature where it can be directly measured on the absorption spectra. This result implies that at  $M_S$  the transformed regions are in the fully transformed martensitic structure, as in the Cu-Zn-Al alloy. This situation should be contrasted to that of Ni-Al, where one observes the formation of nuclei of martensite with an incomplete degree of deformation, whose growth is accompanied by a progressive distortion up to the fully transformed structure.<sup>7</sup> This different behavior could be qualitatively understood on the basis of the different elastic properties of noble-metal and Ni-Al alloys. The bulk modulus of Ni-Al alloys is about 40% higher than in noble-metal CsCl alloys (i.e.,  $1.11 \times 10^{12}$  dyne/cm<sup>2</sup> in Cu<sub>56</sub>Zn<sub>43</sub> compared to  $1.66 \times 10^{12}$  dyne/cm<sup>2</sup> in NiAl<sup>21</sup>). This higher bulk modulus could hinder the nucleation in the austenite matrix of a fully transformed martensite with different volume, and favor the formation of an intermediate phase.

The results for the fraction of martensite as a function of the temperature are reported in Fig. 4. The transformation is characterized by an explosive nucleation of about 15% of martensite at  $M_S$  followed by a "rapid" growth, up to an amount of about 75% of martensite present at the temperature  $M_F$  as defined on DSC. After the initial rapid growth, the transformation continues on decreasing  $T$ , with a lower rate. The slow residual transformation occurring below 130 K cannot be observed by DSC, being its rate of transformation too small to give a detectable latent heat of transformation.

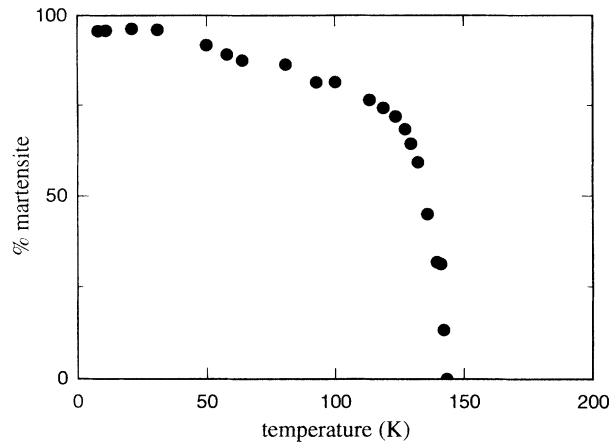


FIG. 4. Fraction of martensite as a function of temperature as obtained by deconvolution of the  $^{113}\text{Cd}$  absorption line.

It is noted that our method allows us to detect subtle memory effects in the thermoelastic cycle. In fact one can observe a small discontinuity in the growth path (see Fig. 4) around the liquid nitrogen temperature, due to the thermal cycling between room temperature and the liquid nitrogen temperature performed 20 times before the NMR measurements. The cycling temperatures were chosen on the basis of the DSC data for the transformation temperatures that give a temperature  $M_F=130$  K. At 77 K, however, the transformation is not completed and, after an overcooling due to the stabilization of the transformation path down to liquid nitrogen temperature, it continues up to a presence of more than 90% of martensite.

## V. CONCLUSION

NMR parameters of  $^{63}\text{Cu}$ ,  $^{113}\text{Cd}$ , and  $^{109}\text{Ag}$  are sensitive to the change of atomic coordination and of electronic structure occurring at the MPT in a Cu-Zn and a Ag-Cd alloy. These changes are remarkably similar to those observed at the MPT in a ternary Cu-Zn-Al shape memory alloy, and affect the value of the Knight shift in the same way at all the crystallographic sites of the alloys. Accurate band-structure calculations or complementary measurements would be necessary in order to quantitatively analyze the results in terms of change of the electronic density of states and of the symmetry of the wave function at the Fermi level.

The difference of resonance frequency in the two phases has been utilized to construct with high precision the transformation curve in the Ag-Cd alloy. We observe an explosive nucleation of martensite at  $M_S$ , followed by a slow growth that continues at a very low rate for about 100 K below the  $M_F$  temperature as determined by DSC. The sensitivity of NMR in the detection of this sluggish transformation relies on the fact that at each temperature the analysis of the NMR spectra gives an absolute determination of the volume ratio of the two coexisting phases, independently of the rate of the transformation as a function of temperature.

The martensitic phase appearing at  $M_S$  is completely transformed, as observed also in the Cu-Zn-Al MPT. This situation differs from that observed in Ni-Al, where the transformation is produced by a progressive distortion of the lattice from an intermediate structure to the fully transformed martensite. It would be interesting to try to correlate the different behavior of the structural transformation in Ni-Al and in noble-metal alloys to the different behavior of the Knight shift and magnetic susceptibility at the MPT.

No anomalies are recorded at the MPT in the relaxation-rate measurements for both  $^{63}\text{Cu}$  and  $^{113}\text{Cd}$ .

This situation is different from that of Cu-Zn-Al alloys where an enhancement of about 20% was observed for  $^{63}\text{Cu}$  and  $^{27}\text{Al}$ . The lack of this effect should be ascribed to the absence of suitable electronic fluctuations able to enhance the standard relaxation mechanisms.

#### ACKNOWLEDGMENTS

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