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АННОТАЦИЯ

Применялись два из методов селективного усреднения в спиновом пространстве: двухимпульсный метод Carr-Purcell и метод Carr-Purcell-Meiboom-Gill для исследования ЯМР-спектров ядер ^{31}P в аморфных сплавах $Ni_{78}P_{22}/Ni_{27}Cu_{73}/_{82}P_{18}$ и $Ni_{80}P_{14}B_{6}$.

KIVONAT

A spin-térbeli szelektiv átlagolási módszerek közül kettőt, nevezetesen a két impulzusos Carr-Purcell, valamint a Carr-Purcell-Meiboom-Gill módszert alkalmaztuk a ^{31}P NMR spektrum vizsgálatára az amorf $Ni_{78}P_{22}$, $(Ni_{27}Cu_{73})_{82}P_{18}$ és $Ni_{80}P_{14}B_{6}$ ötvözetekben.

ABSTRACT

Two of the selective averaging methods [1,2,3] in spin-space namely the two-pulse Carr-Purcell and the Carr-Purcell - Meiboom-Gill methods were applied in the ^{31}P NMR spectroscopy of $Ni_{78}P_{22}$, $(Ni_{27}Cu_{73})_{82}P_{18}$ and $Ni_{80}P_{14}B_6$ amorphous alloys.

INTRODUCTION

The ^{31}P NMR spectrum of the non-magnetic Ni-P and related amorphous alloys consists of several contributions of different origin [4]. The geometrical arrangement of the nuclei and the electronic structure are reflected in one or the other of these contributions. Deconvolution of the NMR spectrum and the interpretation of these contributions are the ultimate goal of the NMR work. Pulsed NMR, namely the coherent averaging procedures give some up-to-date possibilities.

The Hamiltonian describing the ^{31}P spin interaction with its surrounding is

$$\bar{H} = \bar{H}_E + \bar{H}_{II} + \bar{H}_{IS} + \bar{H}_S + \bar{H}_L$$

where $\bar{H}_E$ is the Zeeman interaction with the external fields $\bar{H}_o$ and $\bar{H}_1$, $\bar{H}_{II}$ is the direct and indirect dipolar interaction among resonant spins (^{31}P), $\bar{H}_{IS}$ is the same interaction between resonant and nonresonant (Cu,B) spins, $\bar{H}_S$ contains all the shielding Hamiltonians (chemical shift, Knight-shift) and $\bar{H}_L$ describes the spin-lattice interaction. If an experiment is performed during a time much shorter than the appropriate spin lattice relaxation time (T_1 in laboratory, $T_{1\rho}$ in rotating frame, respectively) then we may ordinarily ignore $\bar{H}_L$. In high magnetic field those parts of the internal Hamiltonians which commute with $\bar{H}_o$ contribute in first order to the spectrum: they are the secular parts. The secular dipolar interaction among resonant spins, $\bar{H}'_{II}$ being a quadratic function of the spin variable, in invariant under a 180^{o} rotation, i.e. cannot be inverted by a 180^{o} rf pulse. The $\bar{H}'_{IS}$ and $\bar{H}'_{S}$ terms are linear function of the I spin variables, so they have the same rotational symmetry properties as the term of Zeeman Hamiltonian describing the effect of an inhomogeneous external magnetic field. These terms give a well defined echo after a 90^{o} - τ - 180^{o} pulse sequence, but the damping of the echo refocused by a 180^{o} pulse is independent of any terms linear in the ^{31}P spin variable $\bar{I}_{Z}$. In particular, shielding terms and the static part of the heteronuclear dipolar term $\bar{I}_{Z}\bar{S}_{Z}$ are averaged out at time 2τ.

EXPERIMENTAL

The two-pulse Carr-Purcell (A) and the Carr-Purcell-Meiboom - Gill (B) pulse sequence and the form of response to these pulses are shown on *Fig. 1*.

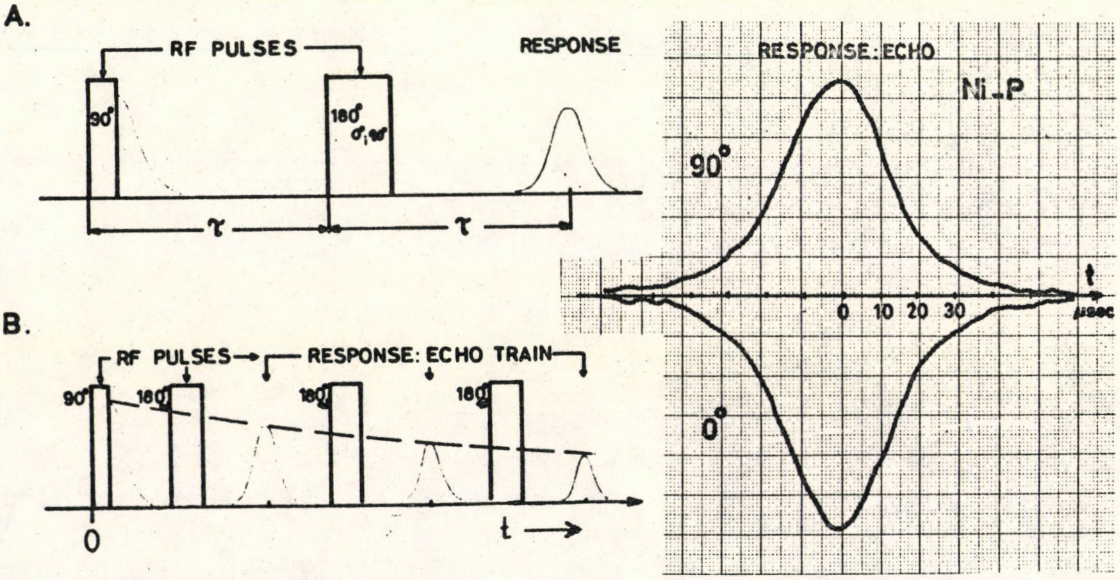

Fig. 1. Pulse sequences and responses. 90^{o} and 180^{o} denote the pulse widths; the second pulse in A is in phase or in quadrature with the first one, in B the first is in quadrature with all the others.

The $Ni_{78}P_{22}$ amorphous alloy was prepared by electrodeposition, the other two alloys by splat-cooling [5]. The measurements were done at 36 MHz by a Bruker SXP 4-100 pulse spectrometer.

RESULTS AND DISCUSSION

By observing $90^o - \tau - 180^o$ echoes with various values of τ, it should be possible to make a direct determination of M_2^{PP}, the resonant spin contribution to the total second moment [6] using

$$E(\tau) \sim \exp(-M_2^{PP}\,\tau^2/2)$$

empirical formula. *Figure 2* shows our results on the amorphous alloys studied in this work. Further results of the measurements on M_2^{PP} in amorphous Ni-Cu-P alloys as a function of the Ni/Cu ratio are presented in Ref. [7].

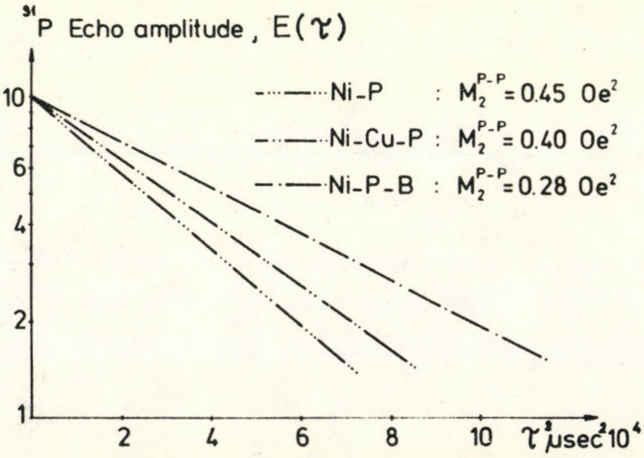

Fig. 2. Semi-log plot of echo amplitudes versus τ^2 using the method A and the second moment M_2^{PP} for our alloys

The CPMG method compensates for damping of the echo envelope not only due to inhomogeneous broadening but also due to rf. inhomogeneity; and what is more important, it acts in first approximation as a spin locking pulse with the effective field

$$H_{1e} = H_1 t_w\,(2\tau)^{-1},$$

providing that echoes do not decay substantially through homogeneous broadening during 2τ which is the time separation between the 180° pulses.

There is no proper theory for amorphous materials and therefore some closely related examples are mentioned from the literature [8] connected with mostly homogeneous solid echo trains. In these cases the echo damping can be described by a single exponential decay characterized by a time constant which approximates the spin lattice relaxation time in metals.

Engelsberg et al. [6] found a double exponential decay in InP, and the first, faster decay was attributed to the cross-relaxation between the resonant (^{31}P) and non-resonant (In) spin systems.

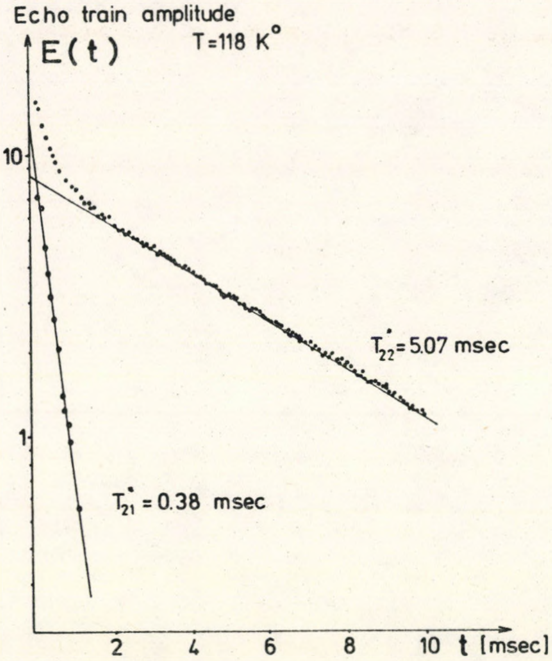

Fig. 3. Semi-log plot of CPMG (method B) echo train for the Ni-P amorphous alloy versus time t. Time separation between the 180° pulses was 80 μsec.

We demonstrate our CPMG results in *Fig. 3*. The decay curve of every investigated alloy shows double exponential character, in spite of the fact that Ni-P represents a system of single spin species and the other two alloys are approximately two-spin species systems. The first trial to interpret our results in *Fig. 3* was the relation

$$E(t) = A_1 \exp\left(-\frac{t}{T^{*}_{21}}\right) + A_2 \exp\left(-\frac{t}{T^{*}_{22}}\right),$$

which was based by Zimmerman and Brittain [9] for two-fraction systems without exchange. It has proved useless because the A_1, A_2, T^*_{21}, T^*_{22} parameters depend on the experimental circumstances.

To demonstrate the effectiveness of the applied selective averaging method, results for the ^{31}P resonance are given in Table 1 in the form of equivalent linewidth and line shape.

Table 1

Method	Echo	CP Two-pulse	CPMG	
			First part	Tail
Line shape	~Gaussian	Gaussian	Lorentzian	Lorentzian
Linewidth [Oe]	12	1.34	0.33	0.04

Fig. 4 shows the T^*_{22} values as a function of the separation time between the 180° pulses for Ni-P, representing the tendency of $T^*_{22} \rightarrow T_1$ (or $T_{1\rho}$) as the separation time goes to zero.

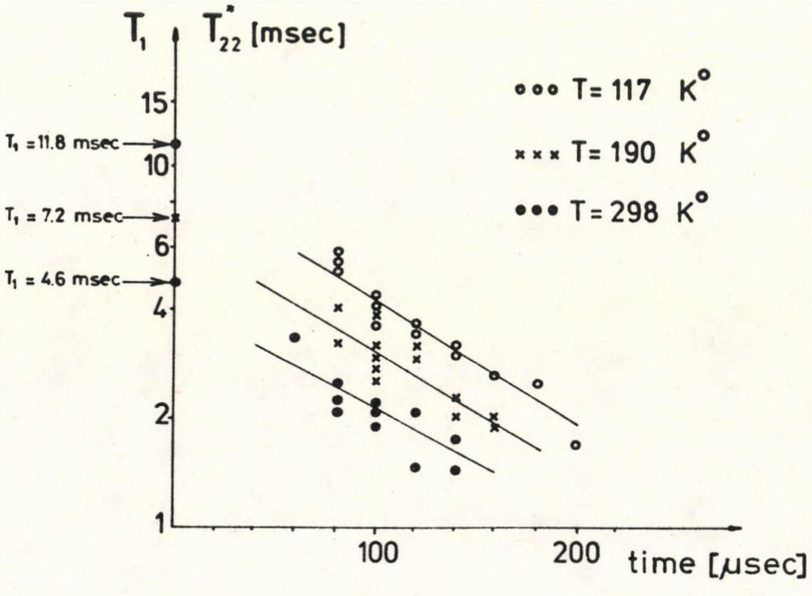

Fig. 4. ^{31}P *transversal relaxation time* T^*_{22} *versus time between the* 180° *pulses in Ni-P,* T_1 *at different temperatures*

CONCLUSIONS

Using the two-pulse Carr-Pucell echoes the second moment among ^{31}P spins M_2^{PP} were directly determined for Ni-P, Ni-Cu-P and Ni-P-B amorphous alloys.

The CPMG echo trains show double exponential character in the consequence of coherent averaging in the spin space (not excluded the stochastic averaging in real space); but the interpretation requires further experimental and theoretical work.

Both methods applied first in the research of amorphous alloys has proved to be useful.

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