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АННОТАЦИЯ

Сняты ЯМР-спектры ядер ^{63}Cu и ^{65}Cu в аморфном сплаве Ni-Cu-P с помощью техники поточечного измерения спинового эха и определены времена спин-решеточной релаксации возбуждением спинового эха при помощи как 180^{o}-ого импульса, так и насыщающей "гребенчатой" серии импульсов. Результаты были сравнены с соответствующими параметрами ЯМР-спектра ядер ^{31}P. Сделан вывод о том, что квадрупольное расширение является преобладающим фактором в ЯМР-спектре обоих изотопов Cu, и за спин-решеточную релаксацию этих ядер отвечает механизм типа Корринга.

KIVONAT

^{63}Cu és ^{65}Cu NMR spektrumokat vettünk fel egy amorf Ni-Cu-P ötvözeten a spin echok pontról-pontra történő mérésével,és meghatároztuk a spin-rács relaxációs időket a 180^{o}-os impulzus-spin echo és a telitő fésü-spin echo sorozatok segitségével. Az eredményeket összehasonlitottuk a ^{31}P NMR spektrum megfelelő paramétereivel. Azt a következtetést lehetett levonni, hogy a kvadrupól kiszélesedés a döntő tényező mindkét Cu izotóp NMR spektrumában és a Korringa-tipusu mechanizmus felelős ezen atommagok spin-rács relaxációjáért.

ABSTRACT

^{63}Cu and ^{65}Cu NMR spectra were recorded on an amorphous Ni-Cu-P alloy using the point-by-point spin echo technique and the spin-lattice relaxation times were measured by the 180^{o} pulse-spin echo and the saturation comb-spin echo sequences. The results were compared with the corresponding parameters of the ^{31}P NMR spectrum. It was concluded that the quadrupole broadening is the dominant factor in the NMR spectra of both Cu isotopes and the Korringa-type mechanism is responsible for the nuclear spin-lattice relaxation.

INTRODUCTION

The Ni-Cu-P system prepared by the melt quenching method is one of the non-magnetic amorphous alloys in which three nuclear magnetic resonance (NMR) spectra, namely that of ^{31}P, ^{63}Cu and ^{65}Cu nuclei can be detected.

Both copper isotopes have a nuclear spin I = 3/2 and, consequently, nuclear quadrupole interaction can exist at the metallic sites in contrast to the ^{31}P nuclei with I = 1/2. As the information obtainable from scattering measurements is restricted to correlation functions, data on structure-sensitive physical quantities are always welcome. The quadrupolar broadening of the NMR lines is especially attractive from this point of view, because a) it is sensitive to the local symmetry; b) the electric field gradient (EFG) can be estimated by some assumptions; c) the asymmetry parameter of the electric field gradient tensor $\eta = (V_{xx}-V_{yy})/V_{zz}$ is dimensionless and so even a simple point-charge approximation may be expected to be appropriate for its estimation.

The study of quadrupole effects has already proved to be useful in determining the local symmetry around the glass-former sites in amorphous alloys [1]. In the present paper ^{63}Cu and ^{65}Cu NMR spectra are given for a Ni-Cu-P amorphous alloy. This is the first report on quadrupole effects at the metal site in metal-metalloid type metallic glasses.

On the other hand, spin-lattice relaxation time (T_1) measurements inform us about the dynamical interaction between the nuclear spin system and the lattice. In metallic substances the dominant contribution to the spin-lattice relaxation originates from the interaction of nuclear spins with the conduction electrons (Korringa-type relaxation). Therefore, the spin-lattice relaxation time is a quantity which is sensitive to the electronic structure.

EXPERIMENTAL

The amorphous $(Ni_{0.27}Cu_{0.73})_{82}P_{18}$ alloy was obtained by melt quenching and sandwich-type samples were prepared from the ribbons [2].

The measurements were performed on a Bruker SXP 4-100 pulse spectrometer at 23.8 MHz frequency at room temperature. The NMR spin echo spectra were recorded and the spin-lattice relaxation times were measured on the ^{31}P, ^{63}Cu and ^{65}Cu nuclei in the above alloy sample. This paper deals mainly with results obtained on the two copper isotopes. Detailed ^{31}P NMR results on amorphous $(Ni_{1-x}Cu_x)_{80}P_{20}$ alloys ($0 \leq x \leq 0.77$) are given in a separate paper [3].

RESULTS

The pulse sequence $90^o - \tau_o - \beta_\varphi$ consisting of two pulses with the phase shift φ was used for studying the spin echoes on the copper nuclei. The length of the first (90^o) pulse was about 4 μsec. The pulse separation time τ_o was kept constant at 120 μsec. Fig. 1 shows the ^{63}Cu echo amplitude as a function of the length t_β of the second pulse with $\varphi = 0^o$. The position of the first maximum corresponds approximately to a rotation angle $\beta = \gamma H_1 t_\beta \simeq 55^o$

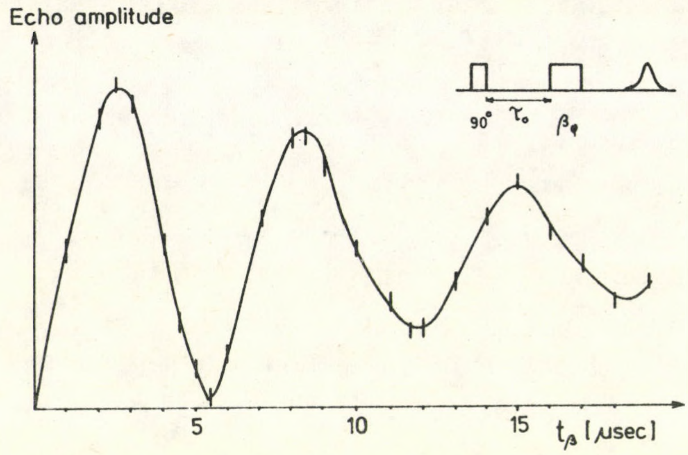

Fig. 1. Echo amplitude as a function of the second pulse length t_β with $\varphi=0^o$ for the ^{63}Cu nuclei in the amorphous $(Ni_{0.27}Cu_{0.73})_{82}P_{18}$ alloy.

where γ is the gyromagnetic ratio of the resonant nucleus and H_1 is the amplitude of the applied radiofrequency field. The $\beta \approx 55^O$ value shows that the echo is mostly of quadrupolar origin [4]. When the same pulse sequence was applied with the phase shift $\varphi = 90^O$ between the pulses the maximum occured at $\beta = 90^O$ as expected [5]. The same result was obtained on ^{65}Cu nuclei.

In Fig. 2 the ^{63}Cu and ^{65}Cu NMR spin echo spectra in the amorphous $(Ni_{0.27}Cu_{0.73})_{82}P_{18}$ alloy can be seen. The spectra were obtained by measuring the spin echo amplitude as a function of the external magnetic field H_o at a fixed frequency (23.8 MHz). The same spectra were recorded by using either a $\varphi = 0^O$ or a $\varphi = 90^O$ phase shift between the pulses in the pulse sequence $90^O - \tau_o - \beta_\varphi$. The spectrum peaks are similar for the two copper isotopes except the amplitudes which are approximately proportional to their isotopic abundances.

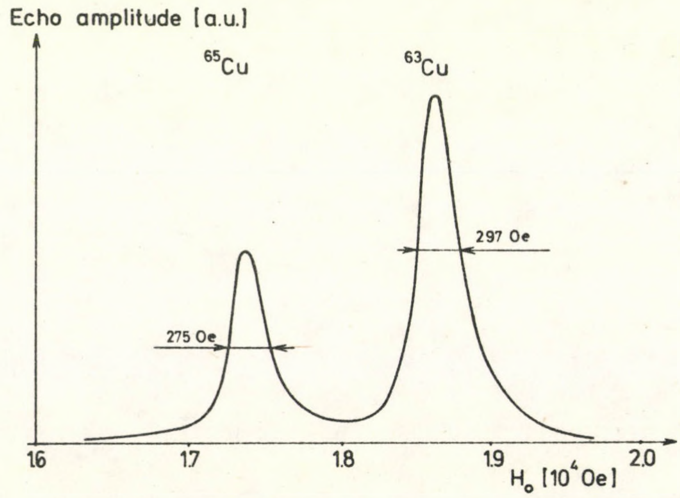

Fig. 2. Quadrupole echo spectra of the copper isotopes in the $(Ni_{0.27}Cu_{0.73})_{82}P_{18}$ metallic glass measured at 23.8 MHz frequency

At present we do not have the necessary data to analyse the observed quadrupole echo spectra of ^{63}Cu and ^{65}Cu nuclei in this amorphous alloy. It is a completely open question whether these spectra originate from first or second order quadrupole effects. Anyway, on the spectra shown in Fig. 2 no fine structure details can be observed, although the instrumental broadening effect should still be considered in details which may be significant if the spectrum of the exciting r-f pulse is not considerably narrower than the spectrum under study.

The spin-lattice relaxation time was measured with the help of the spin echoes. For the preparation of the spin system before generating the echo, two methods were applied. In general, a single 180° pulse is used for the preparation (method B). In the case of strong inhomogeneous broadening, however, a single 180° pulse saturates only a part of the nuclear spin system and a cross relaxation between the saturated and unsaturated part of the spin system contributes to the observed spin lattice relaxation, decreasing T_1. By using the saturation comb-spin echo combination for the preparation (method A) the effect of cross relaxation can be eliminated. Figure 3 shows for both Cu isotopes the spin-lattice relaxation curves and the measured spin-lattice relaxation times obtained by method A at room temperature. As it can be seen from Table I which summarizes the experimental data for all three isotopes, method A is more appropriate for the broad lines of the copper isotopes than method B, whereas for ^{31}P nuclei both give the same T_1 value. In the following, the relaxation times

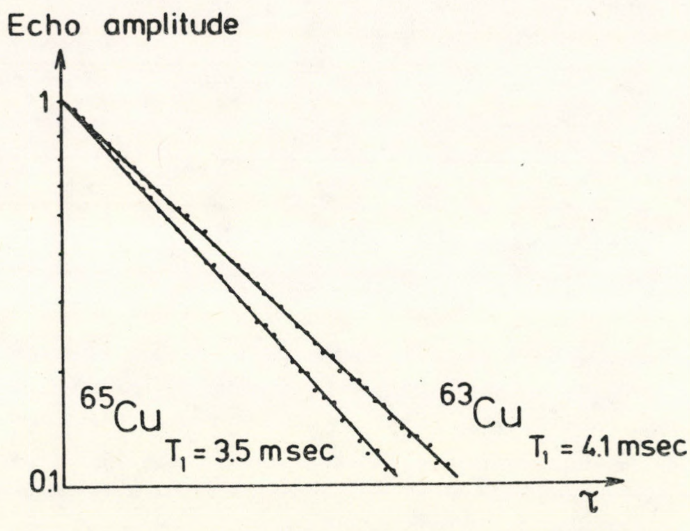

Fig. 3. Semilog plot of the spin-lattice relaxation curves together with the obtained spin-lattice relaxation times for the $(Ni_{0.27}Cu_{0.73})_{82}P_{18}$ amorphous alloy as measured by method A.

obtained by method A will be used for the copper isotopes. It can be calculated from the spin-lattice relaxation time values given in Table I that at room temperature $T_1 \cdot T = 1.05$ K·s for ^{65}Cu and $T_1 \cdot T = 1.23$ K·s for ^{63}Cu nuclei. For comparison we quote the

Table I. Summary of experimental results on the $(Ni_{0.27}Cu_{0.73})_{82}P_{18}$ amorphous alloy

measured quantity \ nucleus		^{31}P	^{63}Cu	^{65}Cu
linewidth (Oe) (±10 %)		10.9	297	275
T_1 (ms) (±5 %)	A	4.7	4.1	3.5
	B	4.7	1.7	1.5

room-temperature results on pure crystalline copper: $T_1 \cdot T = 1.27$ K·s for ^{63}Cu and $T_1T = 1.09$ K·s for ^{65}Cu nuclei [6]. It can also be seen that the ratio of the relaxation times of the copper isotopes $T_1^{63}/T_1^{65} = 1.17$ practically agrees with the inverse ratio of their squared gyromagnetic factors $\gamma_{65}^2/\gamma_{63}^2 = 1.15$. This fact indicates that the spin-lattice relaxation is of Korringa-type, that is, it originates from interactions of the nuclear spin system with the conduction electrons and it does not contain any observable contribution due to quadrupole effects.

CONCLUSIONS

Quadrupolar echoes could be detected on ^{63}Cu and ^{65}Cu nuclei in the rapidly quenched $(Ni_{0.27}Cu_{0.73})_{82}P_{18}$ metallic glass. The quadrupole echo spectra extend over several hundred oersteds. Further experimental work is required to establish whether the origin of this broadening lies in either first or second order quadrupole effects for which a more detailed study of the origin and the signal shape of the echoes is necessary. The spin-lattice relaxation is of Korringa-type, the quadrupolar relaxation does not give a measurable contribution.

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