KFKI-1980-83

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CENTRAL
RESEARCH
INSTITUTE FOR
PHYSICS

BUDAPEST

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To appear in the Proceedings of the Conference on Metallic Glasses: Science and Technology, Budapest, Hungary, June 30 - July 4, 1980; Paper S-02

HU ISSN 0368 5330
ISBN 963 371 729 9

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АННОТАЦИЯ

При комнатной температуре изучались ЯМР-параметры ядер ^{31}P как функции соотношения Ni/Cu в аморфных сплавах $(Ni_{1-x}Cu_x)_{80}P_{20}$ $(0 \leq x \leq 0{,}77)$, полученных быстрым охлаждением из расплава. Измеренные поленезависящие вторые моменты совпадают с полученными ранее результатами модельных расчетов для дипольного расширения. Найдено, что дипольное взаимодействие P-P не зависит от содержания Cu. Даются некоторые данные по сдвигу Найта и времени спин-решеточной релаксации и их краткое обсуждение.

KIVONAT

^{31}P NMR vizsgálatot végeztünk szobahőmérsékleten a Ni/Cu arány függvényében olvadékból gyorshütéssel előállitott $(Ni_{1-x}Cu_x)_{80}P_{20}$ amorf ötvözeteken $(0 \leq x \leq 0{,}77)$. A mért térfüggetlen második momentumok egyeznek a dipól-kiszélesedésre vonatkozó korábbi modellszámolásokkal. A P-P dipól kölcsönhatást a Cu tartalomtól függetlennek találtuk. Közlünk néhány adatot a Knight shiftre és a spin-rács relaxációs időre vonatkozólag is, rövid tárgyalással együtt.

ABSTRACT

The ^{31}P nuclear magnetic resonance was studied at room temperature as a function of the Ni/Cu ratio in rapidly quenched $(Ni_{1-x}Cu_x)_{80}P_{20}$ ($0 \leq x \leq 0.77$) amorphous alloys. The measured field-independent second moments agree with the results of earlier model calculations on dipolar broadening. The P-P dipolar interaction was found to be independent of the Cu content. Some data on Knight shift and spin-lattice relaxation time are also given and discussed briefly.

INTRODUCTION

In this paper a detailed ^{31}P nuclear magnetic resonance (NMR) study is reported on the rapidly quenched $(Ni_{1-x}Cu_x)_{80}P_{20}$ amorphous alloy system for a wide range of the Ni/Cu ratio. The significance of the substitution of Ni by Cu atoms is twofold. The copper atoms have closed shell and, therefore, the replacement of Ni by Cu atoms is expected to cause considerable changes in the ratio of the s and d character of the conduction electrons at the Fermi surface in contrast to the Ni to Pd or Pt substitution [1] where such modifications are not expected. On the other hand, copper nuclei have high magnetic moment, thus they give rise to strong dipolar interactions with the ^{31}P nuclei and this, in turn, results in a relatively high field-independent line-broadening effect, as reported already briefly [2], with respect to the Ni-P [2], Ni-Pd-P, and Ni-Pt-P [1] systems. In the present paper the attention will be focused on the field-independent line-broadening which is de-

termined primarily by the geometrical arrangements of the atoms and the experimental second moments will be compared with the results of earlier model calculations [3]. Those of the ^{31}P NMR parameters which reflect merely the electronic structure will be discussed only briefly here.

SECOND MOMENT CALCULATIONS

The field-independent line-broadening of the ^{31}P NMR spectrum originates from dipole-dipole interactions (since I = 1/2 for ^{31}P nuclei, there is no quadrupole interaction). The primary source is the direct dipolar coupling of the nuclear spins which can be further enhanced by indirect mechanisms (pseudo-exchange [4] or pseudo-dipolar [5] interactions) communicated via the conduction electrons. The magnitude of these pseudo-interactions is completely unknown in the present case. On the other hand, the direct dipolar interaction can be calculated by Van Vleck's theory [6] if the atomic coordinates are given. The total direct dipolar second moment M_2^D of the ^{31}P NMR spectrum is given by

$$M_2^D = M_2(P) + \sum_i M_2(X_i) \qquad (1)$$

where $M_2(P)$ is the second moment contribution due to the like ^{31}P spins and $M_2(X_i)$ is that due to the additional, unlike magnetic nuclei (X_i = ^{61}Ni, ^{63}Cu and ^{65}Cu in the present case). The second moment calculations were performed on a DRPHS model cluster generated by a Monte Carlo procedure. The following assumptions have been made: a) P-P nearest neighbours were not allowed; b) Ni and Cu are structurally equivalent having equal diameters and random substitution. It was found that $M_2(Ni) \approx 0.02\ M_2(P)$ and, therefore, the contribution of the nickel nuclei can be neglected. Further details of the model calculations are described elsewhere [3].

EXPERIMENTAL

The amorphous $(Ni_{1-x}Cu_x)_{80}P_{20}$ alloy were prepared by rapid quenching from the melt using the Liebermann-Graham technique [7]. Glassy alloys were produced in the concentration range $0 \leq x \leq 0.77$.

The ^{31}P NMR measurements were performed on a home-built continuous wave (CW) spectrometer and on a Bruker SXP 4-100 pulse spectrometer.

The field-dependence of the CW absorption derivative peak-to-peak linewidth δH could be well fitted by the formula [8]

$$(\delta H)^2 = (\delta H_o)^2 + (k_1 \cdot H)^2 \qquad (2)$$

where δH_o is the field-independent linewidth contribution, the parameter k_1 characterizes the strength of the field-dependence and H is the external magnetic field. As discussed in Ref. [3] the line shapes are very close to the Gaussian and therefore, the approximation

$$M_2^G = (\delta H_o)^2/4 \qquad (3)$$

was used to obtain experimental field-independent second moments from the extrapolated δH_o values. The extrapolation procedure may result in large relative errors for M_2^G if k_1 is high and δH_o is low. This is the case in Ni-P alloys but alloying with Cu changes the parameters favourably and makes the extrapolation reliable.

The second moment M_2^G includes both P-P and P-Cu interactions. On the other hand, with the help of coherent averaging techniques one can measure interactions between ^{31}P nuclei separately. The P-P dipolar second moment M_2^{P-P} was measured by the two-pulse Carr-Purcell method described in details in Ref. [9].

RESULTS AND DISCUSSION

The measured and calculated second moments of the ^{31}P NMR spectrum are plotted on Fig. 1 as a function of the Cu content in amorphous $(Ni_{1-x}Cu_x)_{80}P_{20}$ alloys. The calculated P-P second moment $M_2(^{31}P)$ is 0.22 Oe^2, and, by assumption, is independent of the Cu content. It can be seen that the second moment M_2^{P-P} is also independent of the Cu content but its 0.4 Oe^2 value is almost twice the calculated one. This excess second moment is definitely greater than the uncertainty of the measured and calculated quantities. It can be concluded therefore, that M_2^{P-P} contains, besides the direct dipolar term $M_2(^{31}P)$, contributions originating from

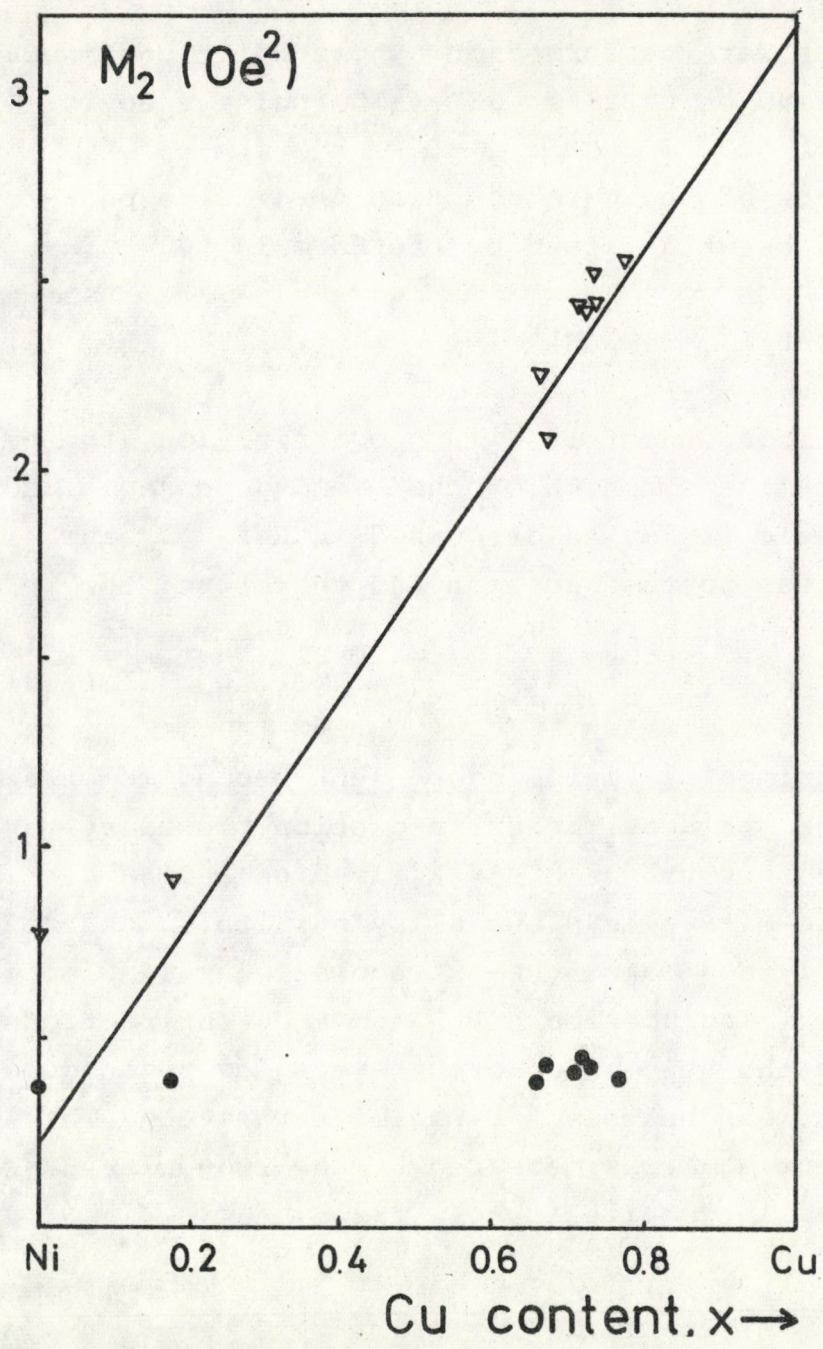

Fig. 1. Field-independent second moments of the ^{31}P NMR spectrum vs Cu content in amorphous $/Ni_{1-x}Cu_x/_{80}P_{20}$ alloys. Experimental: M_2^G/▽/ and M_2^{P-P} /●/; calculated: M_2^D /straight line/ /see text for details/.

indirect interactions, the magnitude of which seems to be independent of the Cu content and comparable to the direct dipolar term. On the other hand, other ^{31}P NMR parameters such as Knight shift and spin-lattice relaxation time are sensitive to the amount of copper introduced into the Ni-P system as it will be given later and therefore, reflect considerable changes in the electronic structure upon alloying. However, in lack of more data on pseudo-interactions in amorphous alloys one cannot conclude at present regarding the origin of the excess second moment observed here.

The straight line on Fig. 1 represents the calculated direct dipolar second moment M_2^D containing the contributions as given by eq.(1). In copper containing alloys the experimental data for M_2^G agree with the calculated values within their error, even if the observed P-P indirect interaction is taken into

account. Data point ∇ for x = 0 may be left out of consideration since it has a high relative error for reasons given in the experimental section.

As discussed at some more length in Ref. [3], pseudo-interactions in amorphous Ni-Cu-P alloys, at least for high enough Cu content, are expected to be very low with respect to the direct dipolar broadening M_2^D. By considering *Fig. 1*, it means that DRPHS model clusters can be effectively used in estimating dipolar broadening in amorphous alloys. One can also conclude that Ni and Cu atoms are randomly distributed on the transition metal sites.

As to the low values of x, it is claimed by Durand et al. [10] that some metals, among them Cu too, do not substitute randomly for the matrix metal atoms in the dilute limit, but behave as glass former and substitute for it. This would mean that there will be no P-Cu first neighbours which, in turn, would considerably decrease the second moment contribution $M_2(Cu)$ and therefore, the total field-independent secont moment of the ^{31}P NMR spectrum. The only composition with low x on Fig. 1 does not allow us to draw any conclusion in this respect, but more accurate measurements on amorphous $(Ni_{1-x}Cu_x)_{80}P_{20}$ alloys with lower Cu content, with the help of some more sophisticated methods [9], will perhaps shed more light to this problem.

Finally, we briefly report on the room temperature measurements of the Knight shift K and the spin-lattice relaxation time T_1. It was found that upon introducing copper into the Ni-P system, K decreases and T_1 increases with increasing Cu content. In a sample with x = 0.73, the spin-lattice relaxation time was measured between T = 100 K and 300 K and the relation T_1T = const. was obtained with $T_1T = 1.43$ K·s. The Korringa ratio $k=K^2T_1T/S$, where $S = 1.605 \cdot 10^{-6}$ K·s for ^{31}P nuclei, was found to change by a factor of two at room temperature in the concentration range studied and approached unity for high Cu content.

The significance of this result can be understood by taking into account that k = 1 is obtained only if non-interacting s-type conduction electrons contribute to the Knight shift and the spin-lattice relaxation [11]. Detailed measurements of K and T_1 will be published elsewhere.

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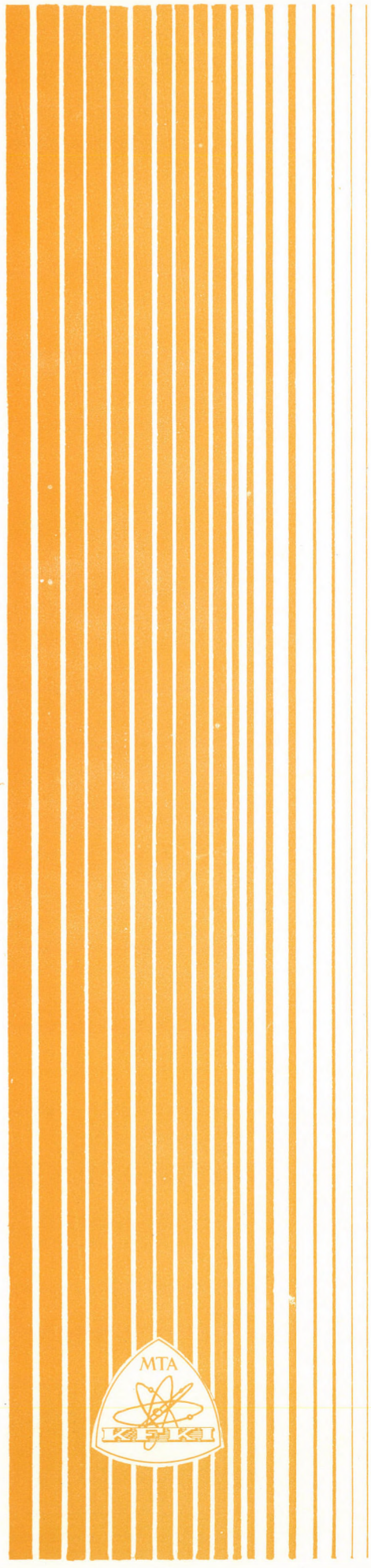

Kiadja a Központi Fizikai Kutató Intézet
Felelős kiadó: Tompa Kálmán
Szakmai lektor: Hargitai Csaba
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Példányszám: 220 Törzsszám: 80-623
Készült a KFKI sokszorosító üzemében
Felelős vezető: Nagy Károly
Budapest, 1980. október hó