PHYSICAL REVIEW B VOLUME 18, NUMBER 5 1 SEPTEMBER 1978

Nuclear-magnetic-resonance studies of amorphous Ni-P alloys

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(Received 27 December 1977)

Measurements of NMR linewidth, Knight shifts, and relaxation time have been made on amorphous Ni-P alloys with phosphorous content between 15% and 25%. Alloys prepared by different techniques (electroplating and chemical deposition) give different Knight shifts, suggesting different local structures. Linewidth measurements support a binary dense random packing of hard-spheres model in which phosphorous atoms have only nickel neighbors.

I. INTRODUCTION

All solids are assumed to be crystalline in their lowest-energy phase, the ultimately stable phase, and glassy (amorphous) materials such as those in the present study must be considered to be metastable. Many of them are stable for all practical purposes at room temperature. Metals are difficult to form in amorphous phases, and the study of such materials is still relatively new. However, during the past few years a great deal of work has been done, primarily on structural and thermodynamic properties.[1,2] Amorphous metal film of the type Ni-P, including Co-P, Au-Si, Ni-Pd-P, and others have been formed by several techniques, including electroplating and splat cooling.

In the present work we have studied the ^{31}P NMR in electroplated and chemically deposited films of Ni-P.[3] From measurements of the Knight shift, spin-lattice relaxation time, and linewidth we infer: (i) that at least two (amorphous) local structures exist with different electronic structures, (ii) that substantial d character exists at the phosphorous site throughout the range of composition under study, and (iii) that the phosphorous coordination is in agreement with the model of Sadoc *et al.*[4]; that is, that phosphorous has only nickel neighbors.

II. THEORY

Most work on amorphous metals has been done in x-ray diffraction studies of structure and in theoretical modeling of structure.

The experimental information (diffraction pattern) has the form of a curve $I(k)$ which, for crystalline material, has a number of sharp peaks at k equal to reciprocal lattice vectors. In the case of amorphous materials (or liquids) $I(k)$ shows only a few broad maxima. The Fourier transform of $I(k)$ gives a real-space radial distribution function (RDF), which in the amorphous case consists also of a few broad maxima.

An early attempt to account for the diffraction results on Ni-P was made in a theoretical model by Doi, Dixmier, and Guinier.[5] This consisted of randomly arranged close-packed layers of atoms; the RDF derived from the model gave reasonable agreement with experiment. Cargill,[2] Bernal,[6] Polk,[7] and others have proposed a model of "dense random packing of hard spheres" (DRPHS) which gives much better agreement with theory. In one version of this, the smaller metalloid atoms are assumed to occupy interstitial sites in the structure. More recently, Sadoc, Dixmier, and Guinier[4] and Bletry and Sadoc[8] have treated a binary DRPHS model which explicitly requires that the metalloid atom have only metal (unlike) neighbors. They support this with a sophisticated diffraction study of Co-P employing x-ray and neutron diffraction techniques (Co-P has a more favorable combination of form factors). Their experimental partial distribution functions (Co-P, P-P, Co-Co) agree with the theoretical model.

Only a few theoretical papers have discussed the electronic structure. Nagel and Tauc[9,10] have proposed a rigid-band model which they say explains the stability of the phase. Stability is associated with a value of k_F such that $2k_F = q_p$ (q_p is that value of q corresponding to the first peak of the structure factor, which occurs for $e/a = 1.7$). They find that a minimum is created in the density of states in the vicinity of E_F. To obtain their results they are required to assume that the structure factor is spherically symmetric. The nature of the bonding was discussed earlier by Polk[7]; in his discussion of the DRPHS he suggests a transfer of charge from metalloid to surrounding metal atoms. The result is an ioniclike contribution to the binding

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energy. Chen,[11] in an examination of stability criteria, studied the atomic volume in a number of systems. From this and from the form of the composition diagram, he argues that in Ni-P covalent bonding must exist, and that short-range order already exists in the liquid.

In a recent letter, Cochrane *et al.*[12] report measurements of electrical resistivity for a series of metallic glasses, including Ni-P, and gives a theoretical treatment based on Anderson's double potential well model. They find they can account for the Kondo-like minimum that exists in all these alloys. The formulation would be more satisfying if we had a detailed atomic scale model for the double well. Zuckerman would appeal to local looseness (or strains or anisotropies) in the lattice.

A recent review by Waseda *et al.*[13] covers the behavior of metallic glasses on heat treatment. A number of stages are observed in the evolution of the "as quenched" amorphous phase to the ultimately stable crystalline material, which may be a mixed phase. For example, Ni-Si-B is found to go through a second amorphous form and a supersaturated fcc crystalline phase, among others. The final product is a mixture of Ni, Ni_3B, and Ni_3Si. Waseda associates the second amorphous phase with relief of local strains and finds that, besides small changes in RDF, there are increases in conductivity and density.

Hines *et al.*[14] have studied the ^{31}P Knight shift, K, for splat-cooled samples of Ni-Pd-P and Ni-Pt-P. They find that K changes with phosphorous concentration in the first case but is independent of relative Ni to Pd or Ni to Pt concentration ratio. They invoke changes in occupation of transition-metal d states to explain the result.

III. PREPARATION

Amorphous Ni-P can be prepared by two different but related techniques, those of electroplating (EP) and chemical (electroless) (EL) deposition, over the same general range of composition.[15] Bagley and Turnbull[16] have also used flash evaporation (from electroplated starting material) in order to obtain a sample of convenient form. The technique of splat cooling, which has been applied to a huge number of binary and ternary materials, is found to be difficult to use in the case of Ni-P.

In the present experiments, $Ni_{1-x}P_x$ films were prepared by both EP and EL techniques over the range $0.15 < x < 0.25$. The techniques and baths used were those used by Brenner.[15] X-ray diffraction patterns were obtained for both types of samples to verify that they were amorphous. Samples were prepared by both techniques at NBS by deposition on Cu foils; the Cu was then dissolved away and the Ni-P was ground to powder in a mortar and pestle. Measurements were made on these samples at NBS using a commercial cross-coil nuclear-induction spectrometer.

The samples made at the College of William and Mary (both EP and EL) were in the form of films plated onto copper cylinders with typical diameters of $\frac{1}{4}$ in. The NMR coil was wound onto the plated cylinder and the techniques employed were those used in metal single-crystal studies.[17] The same results were obtained for Knight shift and linewidth on powder and plated samples.

The analysis of composition was performed by S. Clement of the William and Mary Geology Department using an x-ray fluorescence unit, measuring the intensity of the phosphorous $K\alpha$ x-ray. This measurement was calibrated by conventional chemical analysis. Homogeneity was checked by use of an electron microprobe; variation in composition over the 10-μm thickness was found to be less than 0.01 in x.

IV. RESULTS

We find in electroplated samples a Knight shift K equal to 0.16% and in electroless samples K equal to 0.20% (see Fig. 1). Measurements were also made at 4.2 K; we find $K(\mathrm{EL}) = 0.19\%$ and $K(\mathrm{EP}) = 0.15\%$. In both cases, K is essentially independent of composition above 19% phosphorous. In both materials, as in the crystalline form Ni_3P, it is apparent that the material is a metal, and that the metallic character applies to the phosphorous cell. K was also measured for the crystalline

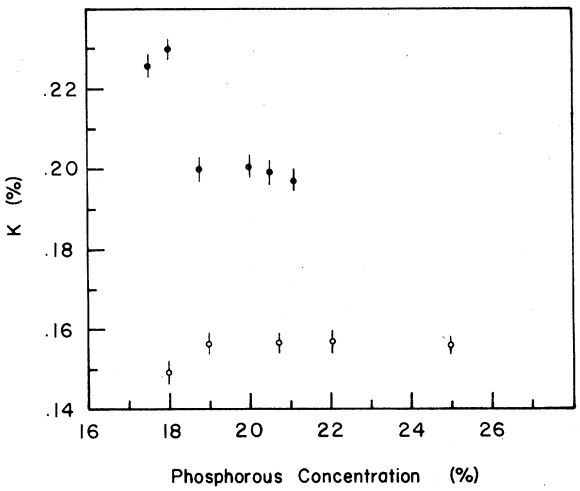

FIG. 1. Knight shift vs phosphorous concentration for electroplated (○) and chemically deposited (●) samples at room temperature. The K values for crystalline Ni_3P and Ni_5P_2 are 0.17% and 0.10%, respectively.

compounds Ni_3P and Ni_5P_2. The values obtained are $K = 0.17\%$ (Ni_3P) and $K = 0.10\%$ (Ni_5P_2).

The independence of composition and the difference of K with method of preparation are both quite puzzling. One might argue in the first case that the short-range environment, including the local electronic structure of the phosphorous atom, does not change with concentration. This would be consistent with the suggestion by Chen[11] that reducing phosphorous content below 25% simply leaves phosphorous vacancies without other changes in structure.

We associate the difference between EL and EP samples with a difference in local structure; that is, this amorphous material is at least dimorphous. For each of these structures there is a well-defined local coordination. (The same is true for amorphous insulators or semiconductors such as amorphous Si).[18] The local electronic structure is then determined by this local structure, that is, by near-neighbor bonding. The difference is local structure is difficult to establish by other techniques. Cargill[19] has published RDF's for electroplated and electroless samples. The difference is very small; furthermore, the curves were obtained by different investigators, making comparison risky.

We believe we have ruled out differences in composition as the source of the difference in K. The starting materials were the same, and the x-ray fluorescence analysis confirms the nickel and phosphorous contents to be as indicated. There was some concern that hydrogen might have been introduced in preparation; however, the proton NMR was not observed. Taking into account the sensitivity of the apparatus, and with reasonable assumptions about width, our sensitivity is such that C_H must be less than 0.1%. Furthermore, low-temperature anneals which would be expected to drive off hydrogen made no change in the NMR spectrum.

We have made some attempts to effect a transformation between what are apparently two metastable phases. In one series of experiments, an anneal of electroless material at 250°C produced a still amorphous but magnetic sample. Leaching converted the material to nonmagnetic form, presumably by removing free nickel. The remaining material was found to have made a discrete change in Knight shift; the new value is the same as that found for electroplated material.

There are indications that the results of annealing or ageing treatments depend very much on details of the combination of the temperature and time being used.[13] As mentioned earlier, there is evidence of metastable crystalline phases existing in similar alloys. It may be that our annealed sample has undergone such a change. We believe that it is still amorphous and it thus could resemble Waseda's second amorphous phase, which has relaxed only the near-neighbor positions. Waseda found an increase in density for a series of amorphous alloys on going from the first to the second amorphous phase (by annealing). Electroplated NiP is more dense than electroless material of the same composition. This suggests that the electroplated phase has a lower energy and supports the identification of it with annealed material.

We observe at 77 K an increase of linewidth for low-phosphorous samples, but essentially no effect for $x > 0.19\%$. The line broadening (for $x \sim 0.15$) is suggestive of the behavior of dilute Cu-Fe, a Kondo system; the contribution of the iron atoms to the local field in that case follows a Curie-Weiss law. It seems very likely that the effect is due to the presence of nickel clusters which behave paramagnetically and give a temperature-dependent linewidth. It would seem that at the present time we cannot specify composition and local structure accurately enough to justify any further statements. We would warn that composition variations constitute a hazard to analysis of NMR results. Unless care is taken, nominally-high-phosphorous samples may contain low-phosphorous regions which lead to false shift and linewidth values.

In both EL and EP films the linewidth is proportional to the applied field, implying that inhomogeneous Knight shift is the primary broadening mechanism. This in turn indicates that the electronic structure is inhomogeneous. The zero field width results from dipolar interactions between ^{31}P nuclei (the ^{61}Ni contribution in negligible). A Van Vleck second moment calculation for a completely random arrangement of nickel and phosphorous nuclei gives a linewidth of 6 kHz. Using the model of Sadoc for the atomic arrangement, wherein phosphorous atoms have only nickel neighbors, we calculate a linewidth of 2 kHz, in reasonable agreement with the experimental results of Fig. 2 (for an EP sample with $x = 0.18$; chemically deposited material has the same zero field width to our accuracy). The field-dependent linewidth is greater in chemically deposited than in electroplated samples. At 10 kOe, typical values are 7 kHz (EP) and 10 kHz (EL). One might argue from this that EP samples have somewhat more local order, in so far as order is related to homogeneity of electronic structure.

A linewidth of 3 kHz was measured for crystalline Ni_3P and crystalline Ni_5P_2. The structure of crystalline Ni_3P is such that the phosphorous atom has only nickel neighbors; this coordination explains the rather small experimental width. Re-

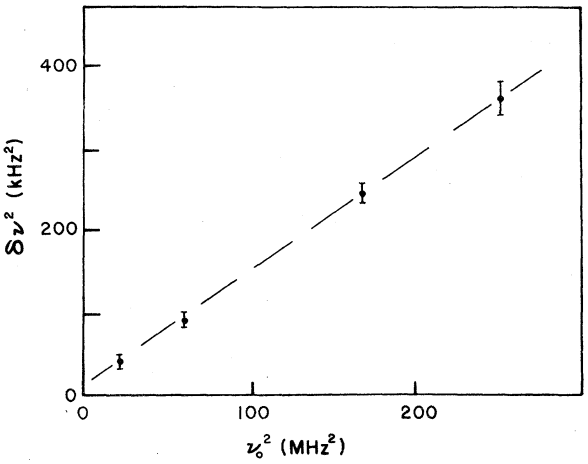

FIG. 2. Linewidth as a function of resonance frequency, plotted quadratically, for an electroless sample containing 0.18% phosphorous. The zero field value is equal to the dipolar broadening; the intercept occurs at 3 kHz.

ferring to the previous paragraph we see that both zero field width and coordination match for crystalline and amorphous cases. This would seem to imply that the same sort of short-range bonding exists in both crystalline and amorphous materials.

Relaxation times (T_1) were measured by pulse techniques for the EL samples of compositions 20% and 21% phosphorous. From the values at 300 and 4.2 K we obtain $T_1T = 1.1$ secK. This value of T_1T together with the K value of 0.21% give a Korringa constant of 3.0, where 1.0 corresponds to pure s electrons. Thus, there is appreciable exchange enhancement for these materials. d-electron effects have been discussed by many authors, who generally break the total χ and Knight shift into s- and d-band effects and orbital effects. We do not attempt to specify the relative size of d-spin and orbital effects (though for Ni alloys orbital effects are probably small). We can say that the Korringa value is evidence of substantial d character at the Fermi surface.

Theory and XPS (x-ray photoelectron spectroscopy) experiments for concentrated alloys of Ni with Cu demonstrate that the Ni d electrons, instead of forming a closed shell, give rise to a virtual bound state and important d-electron effects at the Fermi surface (for concentrations for which the rigid-band model predicts a filled d band). The rigid-band theory of the electronic structure[9] of Ni-P seems to require a minimum in the density of states within or at the upper end of the stability range. Our constant value of K would, rather, indicate that $N(E_F)$ as seen at the P site is insensitive to composition.

ACKNOWLEDGMENTS

We would like to thank I. D. Weisman for his aid in early stages of this work, R. L. Parke for assistance in preparation of samples and in data taking, C. E. Johnson for preparation of electroless samples, and C. J. Bechtoldt for analysis of samples by x-ray diffraction.

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