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Knight shift and spin-lattice relaxation for ^{63}Cu and ^{31}P in amorphous Ni-Cu-P alloys

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Measurements have been made of the Knight shift and the spin-lattice relaxation time for ^{63}Cu and ^{31}P in amorphous $(\mathrm{Ni}_{1-x}\mathrm{Cu}_x)_{80}\mathrm{P}_{20}$ as a function of copper concentration. A negative contribution to the ^{63}Cu Knight shift is observed which is ascribed to polarization of conduction-electron spins by a partially filled *d* band.

INTRODUCTION

It has been found in both crystalline and amorphous alloys based on nickel, palladium, and platinum, that alloying gives a sharp reduction in the density of *d* states at the Fermi surface $N_d(E_F)$. Measurements on glassy alloys of nickel and palladium by such techniques as photoemission, susceptibility, and NMR (Refs. 1–5) have shown a value for $N_d(E_F)$ which is greatly reduced relative to the pure metal. Such results are often interpreted in terms of filling of the transition-metal *d* band (the rigid-band model). Likewise, in nickel alloys, the loss of ferromagnetism on alloying is often assumed to correspond to filling of the unfilled *d* subband.

Recent results by Pease *et al.*[6] on nickel-based glasses (Ni-P and Ni-Pt-P) challenge this model. By a study of the x-ray absorption near edge spectra (XANES), these authors find that the number of empty *d* states in the alloy is not reduced relative to the pure metal. XANES studies of crystalline Ni-Cu (Ref. 7) and Ni-Al (Ref. 8) alloys likewise indicate that there is no decrease in the number of *d* holes even though $N_d(E_F)$ is reduced.

In the present work, we study the NMR Knight shift, *K*, and the spin-lattice relaxation time, T_1, for ^{63}Cu and ^{31}P in amorphous Ni-Cu-P alloys. Our results argue strongly for a model in which the nickel *d* band is not filled; instead the exchange splitting has decreased to zero on addition of phosphorous, so that the alloy is paramagnetic. There is still an appreciable $N_d(E_F)$ which leads to an appreciable susceptibility and a negative contribution to the ^{63}Cu Knight shift.

In presenting the results, we point out that the behavior of the NMR parameters in this case mimic closely the behavior of the same quantities in crystalline Pd-Cu, a system which has been discussed recently by Ebert *et al.*[9]

EXPERIMENTS

The amorphous $(\mathrm{Ni}_{1-x}\mathrm{Cu}_x)_{80}\mathrm{P}_{20}$ alloys used in this work were prepared by melt quenching with $x=0$, 0.06, 0.18, 0.66, 0.72, and 0.77 (alloys with intermediate concentrations $0.2 \leq x \leq 0.6$ could not be obtained in the amorphous state). The thin ribbons so obtained were assembled as a flat sandwich with insulation between layers. NMR measurements were made on a Bruker pulsed spectrometer at $T=77$ and 300 K at a field of 2.0 T.

^{31}P has spin $\frac{1}{2}$ and is 100% abundant so that the line is quite strong. ^{63}Cu gives a strong resonance in copper metal; however, the combination of a large quadrupole moment and the noncubic environment of amorphous metals causes problems. First-order broadening is complete in these alloys and the second-order broadening is quite large. ^{63}Cu NMR studies have been reported for amorphous $(\mathrm{Pd}_{1-x}\mathrm{Cu}_x)_{80}\mathrm{P}_{20}$ and $(\mathrm{Pd}_{1-x}\mathrm{Cu}_x)_{80}\mathrm{Si}_{20}$ alloys[10] as well as for Cu-Zr metallic glasses.[10–12] In all cases, the line is found to be characteristic of a wide range of quadrupole splittings and asymmetry factors. Eifert *et al.*[11] found that the Knight shift obtained by using the line center (peak) was independent of field (whereas the choice of the center of gravity led to a large-field dependence). We follow the same practice as these authors. A previous ^{63}Cu and ^{65}Cu NMR study of the amorphous $(\mathrm{Ni}_{0.27}\mathrm{Cu}_{0.73})_{82}\mathrm{P}_{18}$ alloy has been reported by some of the present authors.[13] A detailed study of the field and concentration dependence of the ^{31}P NMR spectra of the $(\mathrm{Ni}_{0.27}\mathrm{Cu}_{0.73})_{82}\mathrm{P}_{18}$ and $(\mathrm{Ni}_{1-x}\mathrm{Cu}_x)_{80}\mathrm{P}_{20}$ metallic glasses was also described previously.[14]

RESULTS AND DISCUSSION

We have measured the Knight shifts and the spin-lattice relaxation times for ^{63}Cu and ^{31}P in melt-quenched $(\mathrm{Ni}_{1-x}\mathrm{Cu}_x)_{80}\mathrm{P}_{20}$ amorphous alloys $(0 \leq x \leq 0.77)$ at 300 and 77 K, for a field of 2 T. The results are shown in Figs. 1 and 2.

The ^{63}Cu Knight shift is negative for the lowest copper concentration and increases to a value of 0.15% for *x* equal to 0.77. At the same time, $1/T_1T$ decreases from 1.8 $(\mathrm{K\,s})^{-1}$ to 0.15 $(\mathrm{K\,s})^{-1}$. Apparently, a negative contribution to the Knight shift is being lost, and there is a re-

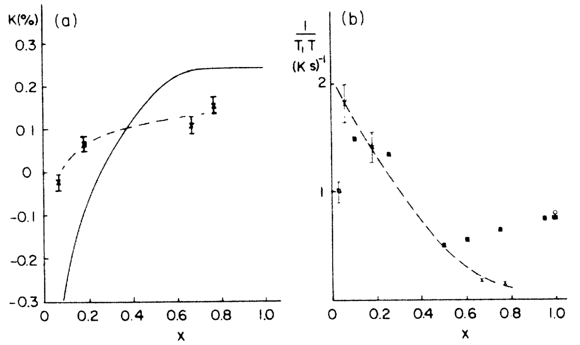

FIG. 1. Experimental data for ^{63}Cu NMR Knight shift, K, and spin-lattice relaxation rate, $1/(T_1T)$, for amorphous $(Ni_{1-x}Cu_x)_{80}P_{20}$ alloys (crosses). For comparison, literature data of ^{63}Cu NMR on crystalline $Pd_{1-x}Cu_x$ alloys are also shown: for K, experimental data from Ref. 17 (——); for $1/(T_1T)$, experimental data from Ref. 18 (□) and Ref. 19 (○), and theoretical values from Ref. 9 (■). The dashed line is intended as a guide for the eye.

lated contribution to relaxation which is disappearing. The same results are obtained at both temperatures.

The behavior of K and T_1 for ^{31}P is more ambiguous. The Knight shift decreases with increasing copper content very much as it decreases with increasing phosphorus content.[5] On the other hand, while $1/T_1T$ decreases initially, the change is small and there is a suggestion of an increase at about x equal to 0.7. We see no temperature dependence of either K or T_1T.

In discussing these results it is useful to compare them to those for ^{63}Cu in Pd-Cu alloys. Pure palladium exhibits a temperature-dependent susceptibility arising from a large d-band density of states which (because of strong energy dependence) is dependent on temperature. This d band is found to polarize the core s electrons and thus to give rise to a temperature-dependent negative Knight shift for Pd.[15] Exactly the same behavior of χ and K is observed for ^{195}Pt in pure platinum.[16] The ^{63}Cu resonance at low copper concentrations in Pd-Cu alloys is found to be shifted negatively because the d electrons polarize the copper conduction electrons.[17,18]

Ebert *et al.*[9] have studied theoretically the ^{63}Cu spin-lattice relaxation in the Pd-Cu system; they find a modest contribution of the palladium d electrons to T_1^{-1}. $1/T_1T$ is found to decrease with the addition of copper due to the decrease of $N_d(E_F)$. It should be pointed out that the value of $1/T_1T$ at very low copper concentration is far smaller than would be expected if there were a common copper-palladium d band with a corresponding copper core polarization (a rigid band).

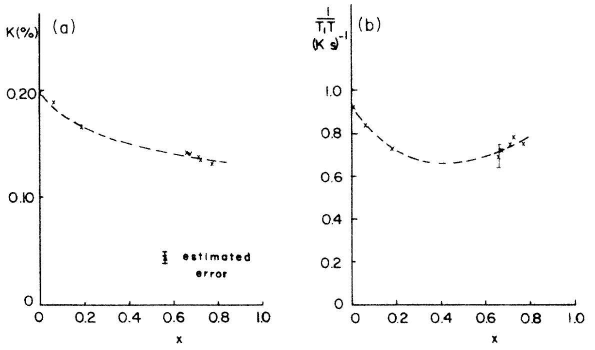

FIG 2. Experimental data for ^{31}P NMR Knight shift, K, and spin-lattice relaxation rate, $1/(T_1T)$, for amorphous $(Ni_{1-x}Cu_x)_{80}P_{20}$ alloys. Lines are drawn as a guide for the eye.

As seen in Fig. 1, the K and T_1 values for ^{63}Cu in the amorphous alloys follow the same behavior as in Pd-Cu.[9,17,18] We interpret the results by assuming that the binary amorphous Ni-P alloy has an appreciable d-band density of states at the Fermi level which accounts for the susceptibility of this alloy and, perhaps, contributes to K and T_1^{-1} for ^{31}P. At low copper concentration the ^{63}Cu NMR exhibits a negative Knight shift contribution due to polarization of copper conduction s electrons by the d band. As copper content increases the negative contribution fades away along with the d-band density of states. The decrease in $N_d(E_F)$ should be, and is, reflected also in a decrease of $1/T_1T$.

Aliaga Guerra[10] has studied the ^{63}Cu and ^{31}P NMR Knight shift and spin-lattice relaxation rates in amorphous $(Pd_{1-x}Cu_x)_{80}P_{20}$ and $(Pd_{1-x}Cu_x)_{80}Si_{20}$ alloys, and his values are very close to the corresponding data for the $(Ni_{1-x}Cu_x)_{80}P_{20}$ alloy series. The concentration range was quite limited ($0.05 \leq x \leq 0.15$); however, he established that the ^{63}Cu Knight shift was well below the pure copper-metal value, indicating the presence of a negative contribution to the ^{63}Cu Knight shift.

We should mention the related results for crystalline Ag-Pd and Ag-Pt alloys. Ebert *et al.*[20] have studied the NMR parameters for the Ag-Pt system (they succeeded in covering the entire composition range by employing rapidly quenched samples). Both the ^{109}Ag and ^{195}Pt resonances exhibit negative K values at the high platinum end of the composition range. The authors assume that the dominant contribution to K for ^{195}Pt comes from core polarization; this term is negative, and it decreases in magnitude along with $N_d(E_F)$ as the Ag content increases. The negative Knight shift for ^{109}Ag is ascribed to conduction-electron polarization rather than to Ag d-band polarization, because it does not give rise to a large relaxation contribution.

Very much the same results are obtained for the ^{109}Ag resonance in Ag-Pd[9,21] alloys. That is, a negative Knight shift is seen for ^{109}Ag in the dilute silver regime, but again there is no large contribution, as from a silver d polarization, to $1/T_1T$. In both Ag-Pd and Ag-Pt, T_1^{-1} for ^{109}Ag is dominated by the s-contact term. Hines *et al.*[5] have studied K and T_1 for ^{195}Pt in amorphous Ni-Pt-P alloys. They find for ^{195}Pt a very small value for K in contrast to the large negative value found for pure platinum, implying a reduced value of $N_d(E_F)$. Following the procedure used by Clogston *et al.*[16] in the case of platinum, they plotted χ versus K in order to isolate the d-band contribution (using the mole fraction of Pt and T as implicit variables). The d-band contribution is much smaller in Ni-Pt-P than in platinum because $N_d(E_F)$ is much smaller; however, the basic mechanism, polarization of Pt core electrons by the Pt d band, must be the same.

Our understanding of the local electronic structure of P atoms in these metallic glasses is much less satisfactory and, up to now, the situation has been rather controversial. We observe here a variation of $K(^{31}\text{P})$ with the increase of the copper content which is very similar to the decrease with increasing phosphorus content.[5] Hines *et al.*[5] argue that the ^{31}P NMR parameters are controlled solely by s-electron contributions. This would mean that changes of K and $1/(T_1T)$ should reflect variation in the s character only. On the other hand, Aliaga Guerra *et al.*[22] concluded that non-s contributions dominate over the s terms.

On the basis of the variation of K and $1/(T_1/T)$ in amorphous $(\text{Ni}_{1-x}\text{Cu}_x)_{80}\text{P}_{20}$ alloys with copper concentration for ^{63}Cu and ^{31}P, we suggest that there is a finite d contribution in the case of the ^{31}P resonance as well. We argue that the behavior of the ^{31}P NMR parameters is related to those for ^{63}Cu, and that the ^{31}P Knight shift contains both s and d contributions. As in the case of ^{63}Cu, the d contribution results from the polarization of the Ni d bands, and it is mediated to the P sites by the conduction s electrons. The observed change of $K(^{31}\text{P})$ with increasing copper content tells us that the d contribution is positive for ^{31}P (there may, of course, also be a variation of the s contribution with composition).

The reduction in the d contribution shows a similar form in the composition dependence of the Korringa ratio $k=K^2T_1T/S$ [here S is the free-electron value of K^2T_1T, and has the values $S(^{31}\text{P})=1.603\times10^{-6}$ K s and $S(^{63}\text{Cu})=3.740\times10^{-6}$ K s]. Figure 3 shows that $k(^{31}\text{P})$ continuously decreases with x and approaches unity for x approaching 1, i.e., the hyperfine interaction of ^{31}P nuclei originates mainly from free noninteracting s electrons in conduction bands at high copper content, whereas the high value of $k(^{31}\text{P})$ at low x indicates the presence of an appreciable d term in $\text{Ni}_{80}\text{P}_{20}$. We note that $1/(T_1T)$ for ^{31}P shows an increase at high copper content rather than a monotonic decrease; we speculate that this upturn for $x>0.5$ reflects similar variations of the s and d contributions as discussed for ^{63}Cu NMR in the crystalline $\text{Pd}_{1-x}\text{Cu}_x$ alloys.[9]

The behavior of $k(^{63}\text{Cu})$ at low copper concentrations is controlled by the variation of K through zero; the low value of K is the result of the cancellation of a negative d term and a positive s term. At high copper content, $k(^{63}\text{Cu})$ increases rapidly and, as $x\rightarrow1$, approaches a value very different from that for pure copper ($k=1.9$), showing the effect of the phosphorus atoms.

It is finally noted that a recent low-temperature specific-heat study[23] of the same $(\text{Ni}_{1-x}\text{Cu}_x)_{80}\text{P}_{20}$ alloys as used here also tends to give evidence for the existence of a considerable $N_d(E_F)$ in the paramagnetic $\text{Ni}_{80}\text{P}_{20}$ amorphous alloy. A magnetic susceptibility study of the amorphous $(\text{Ni}_{1-x}\text{Cu}_x)_{80}\text{P}_{20}$ alloys is planned to further improve our understanding of the electronic structure of these metallic glasses.

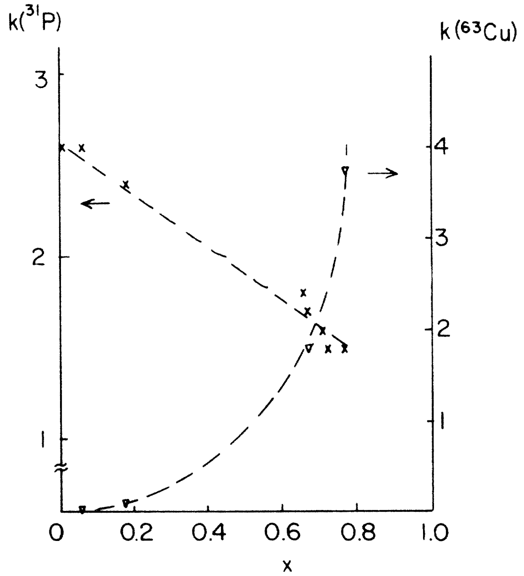

FIG 3. Korringa ratio $k=K^2T_1T/S$ for ^{31}P (left-hand scale, crosses) and ^{63}Cu (right-hand scale, triangles) NMR for amorphous $(\text{Ni}_{1-x}\text{Cu}_x)_{80}\text{P}_{20}$ alloys. The lines are included as a guide for the eye.

CONCLUSIONS

The composition dependence of K and $(T_1T)^{-1}$ for ^{63}Cu in amorphous Ni-Cu-P gives evidence that d holes are present in the base amorphous Ni-P alloy, and that they fill as copper is added. The d band must also play a role in the behavior of K and $(T_1T)^{-1}$ for ^{31}P in both the binary and ternary alloys as the phosphorus or copper content is changed.

According to the model of Beeby,[24] nickel alloyed with simple metals will tend to show a decrease in exchange splitting and loss of ferromagnetism without complete filling of the d band. This model has received support for Ni-Cu alloys in band-structure calculations[25] and XANES studies.[7] The results of recent theoretical work,[26] of XANES (Ref. 6) and specific-heat experiments,[27] and the results of the present study support such a model in the case of amorphous nickel alloys as well. Amorphous Ni-P and the related ternaries may provide a unique opportunity for the study of nearly ferromagnetic systems.

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