ABSTRACT

NMR Knight shift and linewidth measurements are reported for the $^3\text{P}$ nuclei in the metallic glasses $(\text{Ni}_{10.50\text{Pd}_{0.50}})^{100-x}\text{P}_x$ (where $x$ = 16 to 26.5) and $(\text{Ni}_{y}\text{Pt}_{1-y})_{80}\text{P}_{20}$ (where $y$ = 0.20 to 0.68), and both the $^3\text{P}$ and $^{195}\text{Pt}$ nuclei in the metallic glass $(\text{Ni}_{y}\text{Pt}_{1-y})_{75}\text{P}_{25}$ (where $y$ = 0.20 to 0.68). The results are discussed in terms of the amorphous structure, electronic structure, and stability of transition metal + metalloid metallic glasses.

I. INTRODUCTION

Recently, considerable attention has been focused on a class of materials known as metallic glasses [1]. This is due both to a desire for a re-examination of some heretofore fundamental concepts of solids as well as a possibility for a variety of technological applications. Metallic glasses have the general form $(\text{Ni}_{x}\text{Pd}_{y})_{100-x-y}\text{P}$, where $x$ is a transition metal (or combination of transition metals) such as Fe, Ni, Pd or Pt and $y$ is a high valence metalloid such as B, C, Si or P. For the most part, such alloys are prepared by rapid quenching from the liquid state and possess compositions typically ranging from $x$ = 15 to 28 at. % for the Ni metalloid.

This work describes the application of nuclear magnetic resonance (NMR) in the study of the Ni-Pd-P and Ni-Pt-P metallic glass systems. In particular, we have exploited the NMR Knight shift to gain information about electrons at or near the Fermi energy. Spectra obtained from both the transition metal and metalloid elements shed light on the: (1) amorphous structure, (2) electronic structure, and (3) bonding and stability. This in turn leads to a better understanding of the electronic, magnetic and mechanical properties for metallic glasses.

II. EXPERIMENTAL PROCEDURE

NMR Knight shift and linewidth measurements are presented for the $^3\text{P}$ nuclei in the metallic glass systems $(\text{Ni}_{x}\text{Pd}_{y})_{100-x-y}\text{P}$ (where $x$ = 16, 17, 18, 19, 20, 25 and 26.5) and $(\text{Ni}_{y}\text{Pt}_{1-y})_{75}\text{P}_{25}$ (where $y$ = 0.20, 0.30, 0.40, 0.50, 0.60, 0.70 and 0.80), and both the $^3\text{P}$ and $^{195}\text{Pt}$ nuclei in the metallic glass $(\text{Ni}_{y}\text{Pt}_{1-y})_{75}\text{P}_{25}$ (where $y$ = 0.20, 0.30, 0.40, 0.50, 0.60, 0.70 and 0.80). All of the alloys were prepared by a rapid quenching process (plunger and anvil technique) described in detail elsewhere [2]. The foils which resulted from this process were about 50 $\mu$m thick and 2.5 cm in diameter, and were checked by x-ray diffraction to verify their glassy structure.

The NMR measurements were carried out between 77 K and room temperature, for frequencies from 1 to 16 MHz, by utilizing a Varian wideband VF-16 cross coil spectrometer with the related cryogenic accessories. Spectra were obtained from the $^3\text{P}$ nuclei in all the samples and $^{195}\text{Pt}$ nuclei in $(\text{Ni}_{0.50}\text{Pd}_{0.50})_{75}\text{P}_{25}$ only by sweeping the dc field with fixed frequency. The field was calibrated with $^1\text{H}$ ions in solution. Typical NMR spectra (derivatives of the absorption curves) for the $^3\text{P}$ and $^{195}\text{Pt}$ resonances have been illustrated in an earlier paper [3]. It was noted that the lineshapes for $^3\text{P}$ demonstrated some asymmetry in that the low field side was broader. The $^{195}\text{Pt}$ resonance was quite broad and possessed a great deal of intensity in the tails. Some preliminary Knight shift and linewidth measurements have been reported earlier [3,4].

III. RESULTS AND ANALYSIS

A. NMR Knight Shift

Figure 1 shows the observed room temperature $^3\text{P}$ Knight shift (in %), $\kappa$, (defined by the derivative crossover point) as a function of P concentration, $x$, for the $(\text{Ni}_{0.50}\text{Pd}_{0.50})_{100-x}\text{P}_x$ system. Data are shown for a resonance frequency, $\nu$, of 8 MHz. It can be seen that the Knight shift demonstrates a strong decrease as the P concentration increases from $x$ = 16 to 26.5. The dependence is essentially linear and extrapolates to zero Knight shift for $x$ = 40. The variation of the $^3\text{P}$ Knight shift with frequency for the respective $(\text{Ni}_{0.50}\text{Pd}_{0.50})_{100-x}\text{P}_x$ compositions is shown in Figure 2 (closed symbols and dashed lines). It can be seen that all six compositions studied have no detectable frequency dependence within the error. For comparison, the $^3\text{P}$ Knight shift frequency dependence for the $(\text{Ni}_{y}\text{Pt}_{1-y})_{75}\text{P}_{25}$ and $(\text{Ni}_{y}\text{Pt}_{1-y})_{75}\text{P}_{25}$ systems to be discussed below are included (vertical lines with bars); again, no variation with frequency is observed.

Figures 3 and 4 show the observed room temperature $^3\text{P}$ Knight shift as a function of Ni concentration, $y$, for $(\text{Ni}_{y}\text{Pd}_{1-y})_{80}\text{P}_{20}$ and $(\text{Ni}_{y}\text{Pt}_{1-y})_{75}\text{P}_{25}$ respectively. For both systems, the data shown were obtained at 8 MHz. In contrast to the $(\text{Ni}_{0.50}\text{Pd}_{0.50})_{100-x}\text{P}_x$ results, both $(\text{Ni}_{y}\text{Pd}_{1-y})_{80}\text{P}_{20}$ and $(\text{Ni}_{y}\text{Pt}_{1-y})_{75}\text{P}_{25}$ have a Knight shift which remains unchanged within the error over the entire range of Ni concentration ($y$ = 0.20 to 0.68 in the former and $y$ = 0.20 to 0.68 in the latter). This behavior might be expected as a change in concentration would vary the average number of electrons per atom while a change in Ni relative to Pd or Ni relative to Pt would not. As indicated above, and in Figure 2, there is no frequency dependence of the $^3\text{P}$ Knight shift for these systems. The solid vertical lines with bars, at the various frequencies represent the range of shift values for the seven compositions of $(\text{Ni}_{y}\text{Pd}_{1-y})_{80}\text{P}_{20}$ and seven compositions of $(\text{Ni}_{y}\text{Pt}_{1-y})_{75}\text{P}_{25}$. The slight frequency dependences reported earlier were due to very small discrepancies in the NMR standards used to mark field [4]. It is important to note that the shift value characteristic of all the $(\text{Ni}_{y}\text{Pt}_{1-y})_{80}\text{P}_{20}$ alloys is the same as that for $(\text{Ni}_{0.50}\text{Pd}_{0.50})_{100-x}\text{P}_x$ with $x$ = 20. Similarly, the
value characteristic of all the (Ni$_y$Pd$_{1-y}$)$_7$P$_{25}$ alloys is the same as that for (Ni$_{0.50}$Pd$_{0.50}$)$_{100-x}$P$_x$ with $x = 25$. Consequently, a certain degree of similarity in the electronic structure for the three systems is expected. The $^{31}$P Knight shift for all the alloys increased essentially linearly by 0.010% between 77 K and room temperature.

The $^{195}$Pt resonance was observed in the (Ni$_{0.20}$Pd$_{0.80}$)$_{75}$P$_{25}$ sample at 77 K and room temperature. The resonance spectrum is quite broad with a linewidth of about 40 Oe and possessing a great deal of intensity in the tails. The most striking feature of the $^{195}$Pt resonance in the metallic glass is a room temperature Knight shift value, corresponding to the derivative crossover point, of approximately $-0.1\% \pm 0.05\%$. There was no detectable temperature dependence for the $^{195}$Pt Knight shift, although with the broad line, we can only state that any change in shift between 77 K and room temperature is less than 0.05%. This is to be compared with a value of $-3.5\%$ for $^{195}$Pt in pure crystalline Pt. The large negative Knight shift for $^{195}$Pt in Pt metal has been attributed to a dominant core polarization contribution and the resulting positive increase in the Knight shift for $^{195}$Pt in the metallic glass provides strong evidence that the TM d-states are filled which is consistent with a charge transfer from the metalloid to transition metal atoms. A calculation of the resonance intensity and an investigation of the saturation behavior verify that the $^{195}$Pt resonance is indeed characteristic of Pt in the metallic glass and not a small amount of Pt which has formed a second phase or non-metallic phase. Furthermore, the wide linewidth for the $^{195}$Pt resonance suggests a broad distribution in the degree of the d-state filling.

B. NMR Linewidth

Due to signal-to-noise problems arising from a poor filling factor, the $^{195}$Pt linewidth could only be measured in the (Ni$_{0.20}$Pd$_{0.80}$)$_{75}$P$_{25}$ sample at 8 K. As indicated above, the peak-to-peak width was approximately 40 Oe.

The linewidth for $^{31}$P in all the alloys and $^{195}$Pt in (Ni$_{0.20}$Pd$_{0.80}$)$_{75}$P$_{25}$ remained unchanged as the temperature was varied between 77 K and room temperature.

IV. DISCUSSIONS AND CONCLUSIONS

A. Electronic Structure (Density of States)

For all three systems, we attribute the $^{31}$P Knight shift to two principal contributions, i.e. $K = K_1 + K_2$, where $K_1$ is the "direct contact shift:" resulting from a polarization of the conduction s-electrons by the external magnetic field which is communicated to the $^{31}$P nuclei via a contact hyperfine interaction and $K_2$ is the "d polarization shift:" resulting from a polarization of the transition metal d-electrons by the external magnetic field which is communicated to the $^{31}$P nuclei via a s-d interaction that polarizes the conduction s-electrons (together with the contact hyperfine interaction).

### Table I

<table>
<thead>
<tr>
<th>$x$</th>
<th>$c$ (Oe/MHz)</th>
<th>$\delta_2$ (Oe)</th>
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</thead>
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<tr>
<td>16</td>
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<td>1.7</td>
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<td>17</td>
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<td>1.4</td>
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<tr>
<td>26.5</td>
<td>0.31</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Values of $c$ and $\delta_2$ obtained by fitting the linewidth data for (Ni$_{0.50}$Pd$_{0.50}$)$_{100-x}$P$_x$ alloys to eqn. (1).
Values of $c$ and $b_2$ obtained by fitting the linewidth data for $(\text{Ni}_{1-y}\text{Pd}_y)_{100-x}\text{P}_x$ alloys to eqn. (1).

### TABLE II

$$
\begin{array}{ccc}
\gamma & c \text{ (Oe/MHz)} & b_2 \text{ (Oe)} \\
0.20 & 0.42 & 1.3 \\
0.30 & 0.46 & 1.1 \\
0.40 & 0.45 & 1.2 \\
0.50 & 0.46 & 1.4 \\
0.60 & 0.48 & 1.4 \\
0.70 & 0.52 & 0.9 \\
0.80 & 0.56 & 0.9 \\
\end{array}
$$

### TABLE III

$$
\begin{array}{ccc}
\gamma & c \text{ (Oe/MHz)} & b_2 \text{ (Oe)} \\
0.20 & 0.40 & 2.0 \\
0.30 & 0.40 & 1.9 \\
0.40 & 0.40 & 1.8 \\
0.50 & 0.40 & 1.8 \\
0.60 & 0.35 & 1.4 \\
0.70 & 0.31 & 1.3 \\
0.80 & 0.28 & 1.3 \\
\end{array}
$$

### REFERENCES