Reversible effects of temperature on the structure of amorphous NiP

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The influence of temperature on the structure of amorphous NiP was determined by means of x-ray and thermal-expansion measurements. The results compare well with the theoretical predictions for the static x-ray structure factor of an amorphous Debye solid. Observed changes in the structure factor with temperature are of the correct magnitude to explain the temperature dependences of the resistivity of amorphous metals in terms of the Ziman liquid-metal theory; this is taken as further experimental confirmation of the validity of liquid-metal theory for electron transport in these systems.

I. INTRODUCTION

X-ray and thermal-expansion measurements were performed to determine the influence of temperature on the structure of glassy NiP. The results are compared with the predictions of theory for the static x-ray structure factor $S(K)$ of an amorphous Debye solid.[1] No detailed study of this kind is available[2] at present, and our conclusions for NiP are expected to reflect the general behavior of metallic glasses.

The results are of particular interest in the area of electron transport in structurally and compositionally disordered metals and alloys. Previous experimental and theoretical works[3-7] support the use of the Evans, Greenwood, and Lloyd modification[8] of the Ziman liquid-metal theory[9] to describe the resistivity of such systems. In the context of this theory the temperature dependence of the dynamic structure factor determines the temperature dependence of the resistivity. The present structure measurements show that the thermal disordering effects are of the same magnitude as the temperature dependences of the resistivity in metallic glasses, and thus provide further experimental support for this theory.

II. EXPERIMENTAL

The 20- and 25-at.% P samples were prepared from baths and conditions similar to those given by Cargill.[10] Flat plates approximately 2 cm $\times 4$ cm $\times 0.4$ mm and 4-mm-i.d. hollow cylinders were prepared for x-ray diffraction and thermal-expansion measurement, respectively. These were obtained by electrodepositing onto flat copper substrates or hollow copper cylinders which were then dissolved in a chromic-acid–sulfuric-acid solution without affecting the NiP sample.

A. X-ray diffraction

The intensity data were obtained using an automated Phillips diffractometer and XRG 5000 x-ray generator. Molybdenum and copper radiations were used with a scintillation counter, a LiF diffracted beam monochromator, and a pulse-height analyzer.

A hot-plate sample heater was fabricated for x-ray measurements at 22 and 220 °C. This was mounted on a modified diffractometer sample holder. Temperatures were monitored with an iron Constantan thermocouple. Stability during a run was ±2 °C.

The intensity vs 2θ scans were performed in sections to permit frequent checks at reference points before and after a scan to ensure that the count rate remained stable. The counting time intervals were selected to give sufficient accuracy at the peaks and a reasonable total run time (8 to 16 h for a given section of the 2θ range).

As with splat-cooled amorphous metals, we found that irreversible structural relaxations occur upon initial heating of the electrodeposited NiP samples. Such difficulties were avoided by first vacuum annealing the samples between microscope slides for four hours at 220 °C.

B. Analysis of the x-ray data

A computer program provided by Wagner[11] was used to calculate the structure factor (or interference function). The measured intensities were corrected for experimentally determined background and Compton modified radiations, and for polarization. The "high-angle method" was used to convert to electron units $S_{eu}(K)$ which is defined as the ratio of the scattered intensity to the classical intensity from a single electron and where $K = 4\pi (\sin\theta)/\lambda$. The structure factor $S(K)$ is given by

$$S(K) = \frac{[S_{eu}(K) - c_1 c_2 (f_1 - f_2)^2]}{(c_1 f_1 + c_2 f_2)^2},$$

where c_1 c_2, f_1, and f_2 are the respective concentrations and atomic scattering factors of nickel and phosphorus. Defining $F(K) = K[S(K) - 1]$ and $G(r) = 4\pi(\rho(r) - \rho_0)$, we have the relation

$$G(r) = (2/\pi) \int_0^\infty F(K) \sin(Kr) \, dK.$$

$rG(r) + 4\pi r^2 \rho_0$ is the radial distribution function; ρ_0 is the average atomic density.

The background was measured using a beam stop, and the Compton contribution was determined by scattering from an annealed crystalline nickel foil. This automatically eliminates any "Compton down-scattering" which is a function of monochromator geometry, but contains the crystalline thermal diffuse scattering (TDS).[12] The known x-ray Debye temperature permitted an empirical correction for the TDS using $S_{TDS} \propto 1 - e^{-2M}$ for fcc lattices midway between reciprocal lattice points.[13] We recorded the pure nickel background at two temperatures, 22 and 250 °C, to obtain the proportionality constant and the TDS term. The pure nickel Compton contribution was then scaled down by approximately 8% in this region to give corrected values for $Ni_{75}P_{25}$. Empirical corrections were made throughout to account for changes in air scattering and air absorption from heating effects. The resultant $S(K)$ oscillates about unity, and only small oscillations of $G(r)$ about $-4\pi\rho_0$ are seen for $r < 2$ Å which indicates the validity of the procedures employed.

C. Thermal expansion

The Dupont 942 thermomechanical analyzer was used for thermal expansion measurements on the amorphous $Ni_{75}P_{25}$ samples. 1-cm sample lengths were selected to conform to the uniform temperature zone of the furnace. The differential transformer was air cooled to prevent convective heating and resultant hysteresis effects. The system was calibrated with a 99.999%-purity Al cylinder and checked against Pt and Cu standards. Agreement within ±2% of the tabulated expansion coefficients was found.

III. RESULTS

A. Thermal expansion

The thermal expansion of an amorphous NiP cylinder is shown in Fig. 1. Several cycles to 250 °C were recorded in order to demonstrate the structural relaxation effects which occur above 100 °C in the unannealed samples. Similar effects are observed in conventional glasses[14] and in splat-cooled metallic glasses.[15] Creep measurements[16] on amorphous $Ni_{76}P_{24}$ also reveal the presence of these relaxations.

The rapid length contraction in the vicinity of 300 °C is due to cystallization; in this region $\Delta l/l \cong 0.36\%$ giving $\Delta V/V \cong 1.1\%$ which is predicted for metallic glasses.[17]
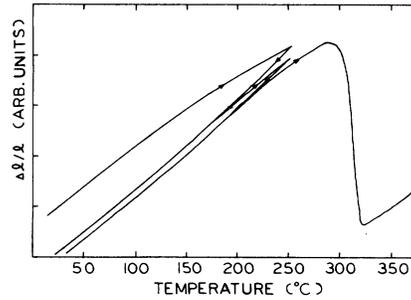
FIG. 1. Thermal expansion of amorphous $Ni_{75}P_{25}$. Structural relaxations are evident in the initial cycles at 250 °C. Length reduction at 300 °C is due to crystallization.

The temperature range of interest for our x-ray measurements is between 20 and 200 °C. The average expansion coefficient α in this range is $14.2 \times 10^{-6}/°C$. For the fully crystallized $Ni_{75}P_{25}$ sample, $\alpha = 14.6 \times 10^{-6}/°C$.

B. X-ray diffraction

The effects of temperature on the first two peaks in the x-ray structure factors of a $Ni_{75}P_{25}$ sample were examined in detail. Both peaks shifted to lower peak positions K_p on heating. Using a least-squares second-order polynomial fit to between 10 and 20 data points in the upper 25% of the peaks, $\Delta K_p/K_p = -0.27\%$ for the first peak, and -0.24% for the second. This is in accord with the assumption of uniform thermal expansion which gives $\Delta K_p/K_p = -\alpha \Delta T = -0.28\%$ using our measured value of α.

The relative changes in the $Ni_{75}P_{25}$ structure factor $\Delta S/S$ due to heating are shown in Fig. 2. The thermal expansion shift was removed using a
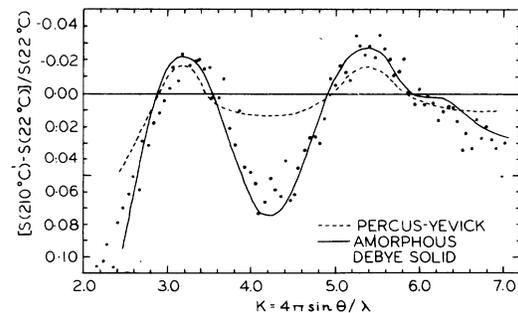
FIG. 2. Relative changes in the structure factor of amorphous $Ni_{75}P_{25}$ on heating from 22 to 210 °C. Data are compared with the theory for an amorphous Debye solid ($\Theta = 340$ K). Also shown are the relative changes in the Percus-Yevick hard-sphere alloy model due to thermal expansion.

variable power spline interpolation function curve fit.[18] The scatter in the data is primarily statistical in origin. The main observations are (i) $\Delta S/S$ is negative in the immediate vicinity of the peaks and positive elsewhere; (ii) the magnitude of $\Delta S/S\Delta T$ is of the order of $-10^{-4}/$ °C at the peaks and generally larger and positive in the peak tails; and (iii) the radiation missing from the peaks appears in the peak tails as indicated by the result that $\sum \Delta S(K) = 0$ within experimental error over this range of K values.

FIG. 3. Comparison of the observed x-ray structure factor of amorphous $Ni_{75}P_{25}$ with the Percus-Yevick hard-sphere model ($\eta = 0.525$). Also shown is the computed A^x (K) assuming a Debye spectrum ($T = 295$ °K).

IV. DISCUSSION

The uniform thermal expansion indicated by the uniform shift in the first two peak positions in $S(K)$ for NiP contrasts with the behavior reported for liquid metals.[19,20] For the latter, because of structural rearrangements, the main peak either remains at its original position on heating or may shift to slightly smaller K_p values while the second peak shifts to larger K_p values. This simpler behavior of amorphous metals, combined with a factor of three or four smaller expansion coefficients, permits convenient simplifications in the analysis of resistivity data. For example, the Fermi sphere diameter $2k_F$ can be assumed to expand or contract to exactly compensate for any peak shifts in the structure factor.[6] This also relaxes the requirement, which exists for liquids,[21] that the resistivity data be recorded under constant-volume conditions for a proper analysis in terms of the Ziman theory. We therefore consider that amorphous metals provide a more straight forward experimental test of the Ziman model than is possible with liquids and have shown, in fact, that it correctly predicts most of the observed temperature dependences in disordered and amorphous alloys over the entire range from $T = 0$ °K.[7]

A theory for the effects of temperature on the structure factors of amorphous Debye solids was given in an earlier paper.[1] For x-ray scattering[22]

$$S(K) = a(K)\exp(-2M) + A^x(K)[1 - \exp(-2M)], \quad (1)$$

where

$$a(\vec{K}) = (1/N)\sum_{m,n} \exp[i\vec{K}\cdot(\vec{m} - \vec{n})],$$

$$A^x(K) = \int_0^1 d(q/q_D)\int \frac{d\Omega}{4\pi}a(\vec{K} + \vec{q}) \quad \text{for } T \gtrsim \Theta,$$

$\exp(-2M)$ the Debye-Waller factor, Θ the Debye temperature, $\vec{q}$ is the phonon wave vector, N is the number of atoms in the sample, and q_D is the radius of the Debye sphere. Since q_D is large relative to the scale of the structural features in $a(\vec{K})$, as a very rough estimate, $A^x(K)$ can be taken

as unity. Equation (1) then reduces to that previously discussed by Cargill,[10] Cote et al.,[23] Nagel,[24] and Wagner et al.[25] For any detailed comparison with experiment however, the computed values of $A^x(K)$ are required. The Percus-Yevick hard-sphere expression[26] for $a(K)$ gives good agreement[6] with the first peak in the measured $a(K)$ for NiP as shown in Fig. 3 and was used to obtain $A^x(K)$. The result, using $\Theta = 340$ K, is also shown in Fig. 3. Since $A^x(K)$ is quite insensitive to the choice of Θ and since metallic glasses all have similar structure factors,[10] $A^x(K)$ in Fig. 3 is considered appropriate for all metallic glasses.

These values of $A^x(K)$ were used in Eq. (1) with $\Theta = 340$ K to calculate the relative changes in structure factor on heating. The measured NiP structure factor served to approximate $a(K)$. The results compare well with the observed $\Delta S/S$ values (Fig. 2) and provide experimental support for the structure factor model described by Eq. (1).

With $A^x(K) = 1$, an effective Debye temperature of ≈ 400 ° K is required to give agreement with experiment. The structure in $A^x(K)$, in effect, reduces Θ and brings it into somewhat better accord with the value (267 K) obtained from low-temperature specific-heat measurements. Among the possible reasons for the remaining descrepancy is that Θ may be temperature dependent so that the high-temperature x-ray Θ is larger. Alternatively, the major contributor to the x-ray scattering is the Ni-Ni partial structure factor,[6] which may have a higher effective Debye temperature than that of phosphorus. Some support for the latter is found in the specific-heat data[27] which shows that Θ is a decreasing function of P content.

The magnitude of $\Delta S/S$ in Fig. 2 and the negative values at the structure factor peaks are both reflected in the resistivity data for metallic glasses. According to the Ziman theory, the temperature dependence of ρ is determined by the temperature dependence of the structure factor so that negative temperature coefficients result from an overlap of $2k_F$ with the peaks in $S(K)$. For transition-metal alloys, the temperature coefficient of ρ is approximately $\Delta S/S\Delta T$ which, from Fig. 2, is

~10^{-4} K^{-1} at the peaks. Positive and negative coefficients of this magnitude are, in fact, typically observed in amorphous metals.

In a previous paper,[6] detailed calculations based on the Evans, Greenwood, and Lloyd modification[8] of the Ziman theory were shown to be in very good agreement with the measured resistivity of amorphous NiP. The magnitudes and composition dependence of the resistivity and the transition from positive to negative temperature coefficients of resistivity were given correctly. In that calculation, the effects of temperature on $S(K)$ were simulated by changing the packing fraction in the Percus-Yevick alloy model[28] to account for thermal expansion. The resultant $\Delta S/S$ values are shown in Fig. 2 for comparison. It was noted that this

might underestimate the thermal-disorder effects. The computed temperature coefficients of resistivity were ~35% smaller than the observed values. As seen in Fig. 2, this is approximately the amount by which our Percus-Yevick values underestimated the actual values of $\Delta S/S$. Use of the actual values would therefore produce excellent agreement between calculated and observed temperature coefficients.

In summary, experimental results on the effects of temperature on the structure of amorphous NiP are in good agreement with the theory for amorphous Debye solids. The data also provide required experimental support for the validity of liquid-metal transport theory for amorphous and disordered alloys.

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