

## Temperature dependence of the resistivity in metallic glasses\*

S. R. Nagel

The James Franck Institute and The Department of Physics, The University of Chicago, Chicago, Illinois 60637  
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The temperature coefficient of the resistivity,  $\alpha$ , of metallic glasses is calculated starting from the same formalism which has been used to calculate the resistivity in liquid transition metals. An explicit equation is derived for the temperature dependence which includes both effects due to the decrease in the static structure factor as well as those due to phonons. The magnitude as well as the explicit temperature dependence of  $\alpha$  is in good agreement with experiment.

### I. INTRODUCTION

In many metallic glasses and disordered alloys the temperature dependence of the resistivity  $\rho$  is anomalous in that over a wide range of temperature the resistivity decreases with increasing temperature. This is in contrast to the normal behavior for ordered crystalline metals, where the temperature coefficient of resistivity  $\alpha = (1/\rho)(\partial\rho/\partial T)$  is large and positive. There have been a number of theories attempting to explain this behavior. However, it has been quite difficult to get a quantitative estimate for the size of  $\alpha$ . In this paper the temperature dependence of the resistivity will be calculated using a formalism<sup>1</sup> originally derived for simple liquid metals by Ziman<sup>2</sup> and extended to include liquid transition metals by Evans *et al.*<sup>3,4</sup> That this theory could also be applied to metallic glass alloys was originally suggested by Sinha.<sup>5</sup> In applying this theory to the glass the temperature dependence is included, as in the case of the liquid, by taking into account the change in the shape of the structure factor,  $S(k)$ , as  $T$  is varied. In order to get an estimate of the importance of this effect on the resistivity, a calculation must be made starting from a microscopic model of a glass. In a liquid,  $S(k)$  will depend quite strongly on temperature and can be calculated using the Percus-Yevick equations.<sup>6</sup> A similar model has been used to describe the glass.<sup>7</sup> However, in the solid the change in  $S(k)$  should be calculated as due to the vibration of ions around their equilibrium positions. We will derive an expression for this change which will involve the inclusion of the Debye-Waller factor.<sup>8</sup> When this is done not only do we get an estimate for the magnitude of  $\alpha$ , but also get the explicit dependence on  $T$ , which is in excellent agreement with available data.

For a transition-metal system the resistivity can be expressed as<sup>1</sup>

$$\rho = \frac{30\pi^3 \hbar^3}{me^2 k_F^2 E_F \Omega} \sin^2[\eta_2(E_F)] S(2k_F), \quad (1)$$

where  $k_F$  and  $E_F$  are the Fermi wave vector and energy, respectively, and  $\Omega$  is the atomic volume.  $\eta_2(E_F)$  is the  $d$ -wave phase shift describing the scattering of the conduction electrons, of energy  $E_F$ , by the ion cores which each carry a muffin-tin potential. In this expression, the temperature dependence of  $\rho$  will be determined by the temperature dependence of  $S(2k_F)$ .

### II. TEMPERATURE DEPENDENCE OF THE STRUCTURE FACTOR

The equilibrium structure factor is

$$S_E(k) = \frac{1}{N} \sum_{i,j} e^{i\mathbf{k}\cdot(\vec{r}_i - \vec{r}_j)}, \quad (2)$$

where  $\vec{r}_i$  is the equilibrium position of the  $i$ th atom and  $N$  is the total number of atoms. At a temperature  $T$  the atoms will be displaced from their equilibrium positions to  $\vec{R}_i = \vec{r}_i + \vec{u}_i$  and the structure factor is given by

$$S_T(k) = \frac{1}{N} \sum_{i,j} e^{i\mathbf{k}\cdot(\vec{r}_i - \vec{r}_j)} e^{i\mathbf{k}\cdot(\vec{u}_i - \vec{u}_j)}. \quad (3)$$

The problem is to calculate the effect on the resistivity of having finite displacements  $\vec{u}_i$ . Care must be taken to include not only the decrease in the intensity of the structure factor but to include the phonon terms as well. Both processes contribute substantially to  $\rho$  and represent competing effects. The first will decrease the resistivity as the temperature is raised and the second will increase it.

We expand the displacements at each site in terms of the  $3N$  real normal modes  $f_{i,\alpha\lambda}$ :

$$\vec{u}_i = \sum_{\alpha,\lambda} \vec{u}_{\alpha\lambda} f_{i,\alpha\lambda}, \quad (4)$$

where  $\lambda$  labels the polarization and  $\alpha$  labels the mode. If we keep all terms to order  $|u_{\alpha\lambda}|^2$ , we can expand Eq. (3) and find

$$S_T(k) = S_E(k) - \frac{1}{2N} \sum_{\alpha, \lambda} (\vec{k} \cdot \vec{u}_{\alpha\lambda})^2 \sum_{i, j} e^{i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)} (f_{i, \alpha\lambda} - f_{j, \alpha\lambda})^2. \quad (5)$$

In order to simplify this expression, we define a transformation relating the normal modes to plane waves:

$$f_{i, \alpha\lambda} = \int d^3q_0 T_{q_0, \alpha\lambda} e^{i\vec{q}_0 \cdot \vec{r}_i} = \int d^3q_0 \int d^3q \frac{1}{\sqrt{2}} [C_{\alpha\lambda}(q_0) \delta_{q_0, q} + C_{\alpha\lambda}^*(q_0) \delta_{-q_0, q}] e^{i\vec{q}_0 \cdot \vec{r}_i}. \quad (6)$$

This form of  $T_{q_0, \alpha\lambda}$  is determined by the fact that  $f_{i, \alpha\lambda}$  was assumed to be real. By substituting Eq. (6) into Eq. (5) and retaining only terms that include  $C_{\alpha\lambda}(q)C_{\alpha\lambda}^*(q)$  we have

$$\begin{aligned} S_T(k) &= S_E(k) - \sum_{\alpha, \lambda} (\vec{k} \cdot \vec{u}_{\alpha\lambda})^2 \left( S_E(k) - \int d^3q S_E(k-q) |C_{\alpha\lambda}(q)|^2 \right) \\ &= S_E(k) e^{-2W(T)} + \sum_{\alpha, \lambda} \int d^3q S_E(k-q) |C_{\alpha\lambda}(q)|^2 (\vec{k} \cdot \vec{u}_{\alpha\lambda})^2, \end{aligned} \quad (7)$$

where  $W(T) = \frac{1}{6} k^2 \sum_{\alpha, \lambda} |u_{\alpha\lambda}|^2$ . The first term contains the usual Debye-Waller factor and the second term represents the phonon contribution. For a crystal the second term reduces to  $Nk^2 |u_k|^2$ .

This expression can be rearranged to give

$$S_T(k) = 1 + [S_E(k) - 1] e^{-2W(T)} - \sum_{\alpha, \lambda} (\vec{k} \cdot \vec{u}_{\alpha\lambda})^2 \int d^3q [S_E(k-q) |C_{\alpha\lambda}(q)|^2 - 1]. \quad (8)$$

The wave vector in which we are interested,  $2k_F$ , is large in metallic glasses and is comparable<sup>9</sup> to  $k_p$ , the position of the first peak in  $S(k)$ . Therefore,  $2k_p - q \gg 0$  for all values of  $q$  near  $q=0$ . Except near  $k=0$ ,  $S_E(k) \gg 0$  as seen in Fig. 1. Therefore, the sum in Eq. (8) will be some weight-

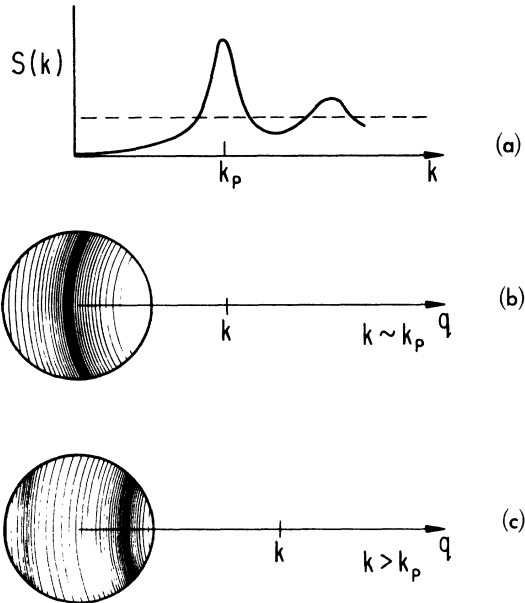


FIG. 1. Schematic diagram of the weighting of  $|u_{\alpha\lambda}|^2$  around  $q=0$  involved in the sum in Eq. (8). In (a) a typical structure factor for a liquid or glassy metal is shown. In (b) (for  $k=k_p$ ) and (c) (for  $k>k_p$ ) the shading represents the weight given to the term  $|u_{\alpha\lambda}|^2$  near  $q=0$ . The shading is proportional to  $S_E(k-q)$ .

ed average of *all* values of  $|u_{\alpha\lambda}|^2$  and will always include some significant fraction of terms near  $q=0$ . The factor  $|C_{\alpha\lambda}(q)|^2$  reflects the fact that  $q$  is not a good quantum number of the system (especially for large values of  $q$ ). This factor has the effect of replacing  $S_E(k-q)$  by an effective structure factor,  $\sum_q |C_{\alpha\lambda}(q)|^2 S_E(k-q)$ , which is even more smeared out than the original one. Actually this will strengthen the assumption we are about to make so we will take the most troublesome case where  $C_{\alpha\lambda}(q) = \delta_{\alpha, q}$ . We have shown this case schematically in Fig. 1. We have shown what the weighting looks like near  $q=0$  for two values of  $k$ :  $k=k_p$  and  $k>k_p$ . The shading represents the height of  $S(k-q)$ . The heavier the shading at a value of  $q$ , the more heavily  $|u_{\alpha, \lambda}|^2 = |u_q|^2$  is weighted in the sum. Even at low temperatures where only long-wavelength phonons are excited, there is strong scattering at large values of  $k$ . This is the remnant of umklapp scattering for large  $k$  in a crystal. However in the glass, as distinct from the crystal, there is always some term in the sum which will bring  $k$  back to  $q=0$ . Thus, the phonon contribution to resistivity is never frozen out in the glass. The relaxation of the requirement of momentum conservation in the "dirty limit" in dilute alloys<sup>10</sup> also changes the low-temperature resistivity behavior in a similar manner.

Since all values of  $q$  are included and since even at  $k=k_p$ , essentially all values of  $|q|$  are weighted equally we can, to a first approximation, neglect the last term. The majority of the phonon contribution is already included in the first two terms. In addition the presence of the factor  $|C_{\alpha\lambda}(q)|^2$

will further smear out the structure factor. The result is a very simple and compact expression:

$$S_T(k) \cong 1 + [S_E(k) - 1] e^{-2W(T)}. \quad (9)$$

Only a knowledge of  $W(T)$  and the magnitude of  $S(2k_F)$  is necessary to calculate the temperature dependence. This approximation is very good at high temperatures since in the Einstein model  $|u_q|^2$  is independent of  $q$  and the average value of  $S(k)$  is 1. In this range of temperature the experimental structure factor is fit quite well<sup>11</sup> by this expression. At low temperatures the error becomes more serious, but the approximation is still reasonable because of the arguments presented above; that is, the phonon contribution never gets frozen out. The above expression also appears to be physically reasonable. Since the average value of  $S_T(k)$  is 1, one would expect that upon changing temperature only  $[S_T(k) - 1]$  should be multiplied by the Debye-Waller factor. Equation (7) also yields the correct high-temperature limit  $S_{T \rightarrow \infty}(k) = 1$ .

We have neglected in this derivation any explicit mention of the inelastic component to the scattering. This could be important at low temperatures. However, if we include energy-transfer effects we find that they enter into Eq. (8) only through  $S_E(k - q)$  and therefore do not enter into Eq. (9) at all. This term we have argued is already very small in the glass and the inclusion of inelastic scattering will only be a small correction to it. The resistivity in the glass is dominated by elastic scattering.

### III. COMPARISON WITH RESISTIVITY DATA

Equation (1) has been shown to give very good agreement with the experimental values of the resistivity for a number of liquid transition metals.<sup>12</sup> It is perhaps surprising that the agreement is so good considering some of the criticisms of it that have been raised.<sup>13</sup> It should also be noted that in many of these materials the mean-free path of an electron is so short that it is questionable whether perturbation theory using a  $t$ -matrix and a structure factor can adequately describe the system since the scattering is obviously strong. Despite these objections we will analyze the temperature dependence of this model using the results of Sec. II. Again good agreement will be found with experiment.

The resistivity as a function of temperature can now be expressed

$$\rho(T) = \frac{30\pi^3 \hbar^3}{m e^2 k_F^2 E_F \Omega} \sin^2[\eta_2(E_F)] \times \{1 + [S_0(2k_F) - 1] e^{-2[W(T) - W(0)]}\}. \quad (10)$$

The temperature coefficient of the resistivity can

be easily calculated:

$$\alpha = \frac{1}{\rho} \frac{\partial \rho}{\partial T} \cong 2 \left( \frac{1 - S_T(2k_F)}{S_T(2k_F)} \right) \frac{\partial W(T)}{\partial T}. \quad (11)$$

We can get a quantitative estimate of the magnitude of  $\alpha$ . In the Debye approximation it is well known<sup>14</sup> that

$$W(T) = \frac{3\hbar^2 k^2 T^2}{2Mk_B \Theta^3} \int_0^{\Theta/T} \left( \frac{1}{e^z - 1} + \frac{1}{2} \right) z dz, \quad (12)$$

where  $\Theta$  is the Debye temperature,  $M$  is the atomic mass, and  $k_B$  is the Boltzmann constant. Since  $\partial W/\partial T > 0$ ,  $\alpha$  is negative if  $S_T(2k_F) > 1$ , and positive otherwise. If  $2k_F$  is near  $k_p$ , the first peak of  $S(k)$ , then a negative temperature coefficient of the resistivity is expected just as in the case of liquids.<sup>1</sup>

The asymptotic temperature dependence of  $W(T)$  is

$$W(T) \cong W(0) + 4W(0) \frac{1}{6} \pi^2 (T/\Theta)^2, \quad T \ll \Theta \\ \cong W(0) + 4W(0) (T/\Theta), \quad T \geq \Theta; \quad (13)$$

where  $W(0) = 3\hbar^2 k^2 / 8Mk_B \Theta$ .

For a typical metallic glass we can make the following estimates,  $\theta \cong 300$  K,  $M \cong 70 \times$  (mass of proton), and  $2k_F \cong 3 \text{ \AA}^{-1}$ . Zener<sup>15</sup> has tabulated the values of the integral in Eq. (9). Using this table and the above estimates we find

$$\frac{\Delta \rho(300 \text{ K})}{\rho} \cong \frac{\rho(300 \text{ K}) - \rho(0 \text{ K})}{\rho(0 \text{ K})} \\ \cong -0.04 \left( \frac{S_T(2k_F) - 1}{S_T(2k_F)} \right). \quad (14)$$

For  $2k_F$  near  $k_p$ , the maximum of  $S(k)$ , the experimental data<sup>16</sup> shows that  $S_T(2k_F) \cong 3$ . We expect for this case  $\Delta \rho(300 \text{ K})/\rho = -0.03$ . This corresponds to the maximum decrease in resistivity that we can expect for this system with the above parameters. In addition, from Eq. (10), we expect the resistivity to vary as  $T^2$  at low temperatures and as  $T$  at high temperatures. Experimental data supports these conclusions.

In the studies of Tangonen<sup>17</sup> on  $(\text{Pd}_{1-x}\text{Cu}_x)_{0.8}\text{P}_{0.2}$ , the resistivity was found to vary quadratically at low temperatures and linearly at higher temperatures. Furthermore the largest value of  $\Delta \rho(300 \text{ K})/\rho$  found was  $-0.03$  for  $(\text{Pd}_{0.5}\text{Cu}_{0.5})_{0.8}\text{P}_{0.2}$ . For other compositions the temperature dependence was less. Oberle *et al.*,<sup>18</sup> have pointed out that this decrease in  $\alpha$  as more Cu is added to the system is what is to be expected if  $2k_F$  approaches  $k_p$ . They observe that the composition region in which  $\alpha$  is large and negative in this system is consistent with data on liquid metals which has been interpreted in terms of the Ziman theory. In Fig. 2 we compare the resistivity data for  $(\text{Pd}_{0.5}\text{Cu}_{0.5})_{0.8}\text{P}_{0.2}$

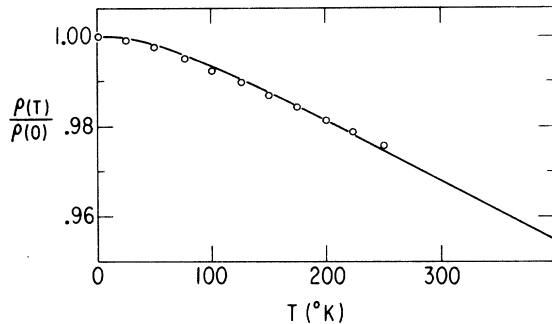


FIG. 2. Resistivity of  $(\text{Pd}_{0.5}\text{Cu}_{0.5})_{0.8}\text{P}_{0.2}$  as a function of temperature normalized to the resistivity at  $T=0$ . The open circles are the data of Tangonen (Ref. 17). The solid line is the theoretical prediction using the estimates of  $M$ ,  $2k_F$ , and  $\Theta$  mentioned in the text.

with our model. The agreement is quite good.

Hasegawa has studied a variety of metallic glasses. He concludes<sup>19</sup> that the normal temperature dependence is quadratic at low  $T$  and linear at high  $T$  as we have found. For  $(\text{V}_{30}\text{Ni}_{27}\text{Pt}_{70})_{75}\text{P}_{25}$  he found<sup>20</sup>  $\Delta\rho(300\text{K})/\rho = -0.015$ . For the Cu:Zr glass (one that contains no metalloids) Szofran *et al.*,<sup>21</sup> and Mizoguchi *et al.*,<sup>22</sup> have found  $\Delta\rho(300\text{K})/\rho = -0.03$  with again the same explicit temperature dependence: quadratic at low  $T$  and linear at high  $T$ . Sinha,<sup>5</sup> who interpreted his data in terms of the Ziman theory, also found a negative value of  $\alpha$  for some compositions. For the system  $(\text{Ni}_{0.2}\text{Pt}_{0.8})_{0.75}\text{P}_{0.25}$  he found  $\Delta\rho(300\text{K})/\rho = -0.02$  and Cote<sup>23</sup> found  $\Delta\rho(300\text{K})/\rho = -0.01$  for  $\text{Ni}_{0.75}\text{P}_{0.25}$ .

It is clear that this theory for the temperature dependence of the resistivity agrees quantitatively with much resistivity data on metallic glasses. The magnitude and sign of  $\alpha$  is easily explained by the appropriate placement of the Fermi wave vector with respect to  $k_p$ . This theory can therefore predict an  $\alpha$  of either sign. This is in contrast to theories<sup>8,19</sup> which give rise to only one sign of  $\alpha$ . The explicit temperature dependence is also in agreement with the data both for alloys that have a positive as well as a negative temperature coefficient  $\alpha$ .

In some glasses,  $\alpha > 0$ . This could be due to several causes: (i) The value of  $2k_F$  could be too far away from  $k_p$  to produce a negative  $\alpha$ . (ii) There could be other competing sources for elec-

tron scattering,  $s$ - $d$  scattering and electron-magnon scattering in magnetic systems.

In one ferromagnetic system, Fe:P, the resistivity was measured<sup>24</sup> both as a function of temperature and concentration. In all cases it was found that the resistivity could be fit to the following form:  $\rho(T) = \rho_0 + \alpha \ln T + bT^2$  for temperature up to 80 K. An important result was that the coefficient  $b$  varied systematically with composition and had a pronounced minimum at the eutectic composition. A recent electronic theory of metallic glass formation<sup>9,25</sup> has associated the eutectic composition with that composition for which  $2k_F \cong k_p$  in the alloy. The contribution of the Debye-Waller factor in decreasing the resistivity as we have described above should also be most pronounced with  $2k_F \cong k_p$  and should thus act to decrease the coefficient of the  $T^2$  term at that composition. Although some other mechanism, possibly spin-wave scattering, produces a large positive contribution to  $b$  in this ferromagnetic alloy the fact that there is a minimum in  $b$  at the eutectic composition is evidence of the validity of the electronic theory.

Finally, a word should be said about the correlation between  $\rho$  and  $\alpha$  discovered by Mooij.<sup>26</sup> By confining his attention to only those systems that had a relatively small temperature coefficient of resistivity, he found that the resistivity tends to be larger in systems which have a smaller value of  $\alpha$ . A similar effect can be seen in the model described above. As  $2k_F$  approaches the peak in the structure factor, the resistivity should increase and the temperature coefficient of resistivity should decrease, becoming negative when  $2k_F$  is sufficiently close to the peak. This raises the possibility that this model can also be used to understand the resistivity in interstitially disordered alloys when Bragg peaks are no longer visible as well as in glasses.

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