

**Nonlinear temperature dependence of the thermopower of amorphous metals**

R. Harris and B. G. Mulimani\*

*Rutherford Physics Building, McGill University, 3600 University Street,  
Montreal, Quebec, H3A 2T8 Canada*

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We demonstrate that the nonlinear temperature dependence of the thermopower in certain amorphous metals and metallic alloys can be explained within the Ziman model. The single generalization required is that the structure factor vary with temperature. We apply our results to hypothetical amorphous zinc and to amorphous Mg-Zn alloys; agreement is very good.

**I. INTRODUCTION**

The study of the thermoelectric power of amorphous metals is frequently placed within the context of what is known about liquid metals. However, measurements of the thermoelectric power of liquid metals have typically been concerned with the magnitude of the effect at a single temperature, usually the melting point of the metal in question, and have seldom been concerned with the temperature dependence of the effect. However, the data which do exist<sup>1</sup> show that in most liquid metals the thermopower is proportional to the absolute temperature: In exceptional cases [Zn, Hg, Tl (Ref. 1)] the data show linear behavior, but with a nonzero intercept at  $T = 0$ .

Some amorphous metals also show a thermopower proportional to the temperature.<sup>2</sup> However, as discussed in a recent review,<sup>3</sup> these are the exceptions, and the data typically show a "knee" at around 50 K or, as in some Mg-Zn alloys<sup>4</sup> or some Metglases,<sup>5</sup> show much more pronounced nonlinearity in the temperature dependence. It is the objective of this article to demonstrate that such nonlinearity arises from a straightforward generalization of the usual Ziman formalism.<sup>6</sup> We first review this formalism, then generalize it, and finally apply it to hypothetical amorphous Zn and to amorphous Mg-Zn alloys.

Theoretical discussion of the thermopower in liquid and amorphous metals has been based upon the Ziman treatment of the diffusion thermopower<sup>6</sup> which, following Mott,<sup>7</sup> links the thermopower  $S$  to the energy derivative of the electron relaxation time  $\tau(E)$ . The appropriate expression is

$$S = -\frac{\pi^2}{3} \frac{k_B^2 T}{|e|E_F} \left. \frac{\partial \ln \sigma(E)}{\partial E} \right|_{E=E_F} \equiv \frac{-\pi^2}{3} \frac{k_B^2}{|e|E_F} \xi T, \tag{1}$$

where  $\sigma(E)$  is the value that the conductivity would have if evaluated at  $T = 0$  with the Fermi level at  $E = E_F$ .  $\sigma(E)$  is thus given by

$$\sigma(E) = \frac{-e^2}{\Omega} D(E) V^2(E) \tau(E). \tag{2}$$

In these expressions the various parameters have their usual meanings: In particular,  $D(E)$  is the density of electron states,  $V(E)$  is the electron velocity, and  $\Omega$  is the atomic volume, and  $\xi$  is the so-called thermoelectric parameter. Ordinarily there is no temperature dependence in  $\sigma(E)$ , so that  $S$  is predicted to be linearly proportional to the temperature  $T$ .

Within the free-electron model, the Ziman expression for  $\xi$  is given by<sup>8</sup>

$$\xi = 3 - 2q - \frac{1}{2}r, \tag{3}$$

where

$$q = |V(2k_F)|^2 S(2k_F) / \langle |V(Q)|^2 S(Q) \rangle, \tag{3'}$$

$$r = \left\langle k_F \frac{\partial}{\partial k_F} |V(Q)|^2 S(Q) \right\rangle / \langle |V(Q)|^2 S(Q) \rangle. \tag{3''}$$

In these expressions,  $S(Q)$  is ordinarily taken to be the static structure factor of the material for scattering wave vector  $Q$ , and  $V(Q)$  is the corresponding matrix element of the scattering potential of one atom.  $k_F$  is the Fermi momentum. The brackets denote an average of the form

$$\langle |V(Q)|^2 S(Q) \rangle = \int |V(Q)|^2 S(Q) 4 \left( \frac{Q}{2k_F} \right)^3 d \left( \frac{Q}{2k_F} \right). \tag{4}$$

In binary alloys, following Faber,<sup>9</sup> the matrix element for scattering from the potentials of the  $N$  ions is written as

$$|V(Q)|^2 = N \{ C_1 V_1^2 S_{11} + C_2 V_2^2 S_{22} + C_1 C_2 [V_1^2 (1 - S_{11}) + V_2^2 (1 - S_{22}) - 2V_1 V_2 (1 - S_{12})] \}, \tag{5}$$

where  $V_1 = V_1(Q)$  and  $V_2 = V_2(Q)$  are the potentials of the two species of concentrations  $C_1$  and  $C_2$ , and  $S_{11}$ ,  $S_{12}$ , and  $S_{22}$  are the three partial structure factors. (For simplicity,  $V_1$  and  $V_2$  are taken to be real.) Following Enderby *et al.*<sup>10</sup> the complexity of this expression is reduced by assuming that  $S_{11} = S_{12} = S_{22}$  and by substituting in (3) to obtain<sup>11</sup>

$$\xi = (C_1 \rho_1 \xi_{\rho_1} + C_2 \rho_2 \xi_2 + C_1 C_2 I) / \rho, \quad (6)$$

where the parameter  $I$  describes the deviations from a simple linear dependence. The parameters  $\rho_1$ ,  $\rho_2$ , and  $\rho$  are the resistivities of the pure components and of the alloy, respectively, and  $\xi_1$  and  $\xi_2$  are the thermoelectric parameters of the pure components. (The expression used by Enderby *et al.*<sup>10</sup> is different from ours, but in fact involves different definitions of the parameters). Thus the concentration dependence is described by three parameters  $\xi_1$ ,  $\xi_2$ , and  $I$ , of which the first two are, in principle, available from experiment. The parameter  $I$  is in principle dependent upon the structure factor, and is therefore dependent upon both temperature and upon  $k_F$ . In the present calculation the temperature dependence is expected to be negligible, because  $S(2k_F) \sim 1$ , and the dependence upon  $k_F$  is small over the range of concentrations employed: Thus,  $I$  is taken to be a constant.

The temperature dependence of the thermopower thus comes about in two ways: First from the proportionality to  $T$  in the basic expression (1), and second from the temperature dependence of the terms  $q$  and  $r$  in Eq. (3). It is the first of these effects which has dominated the literature up to now. The structure factor  $S(Q)$  is, to a first approximation, independent of temperature, so that  $q$  and  $r$  are usually taken as constants. Their values have been the subject of many theoretical papers<sup>12</sup> since only with nonzero  $q$  and  $r$  can the Ziman theory explain the positive thermopowers observed in many liquid metals.

The temperature dependence of  $S(Q)$ , however, does have important consequences for the electrical resistivity of metals, both at temperatures much lower than the Debye temperature ( $T \ll \Theta_D$ ), where a  $T^2$  term is predicted for amorphous metals, and at high temperatures ( $T > \Theta_D$ ), where positive and negative temperature coefficients of resistivity for liquid and amorphous metals can be described.<sup>13</sup> In this paper we investigate the effects of the temperature dependence of  $S(Q)$  on the thermopower: We find them to be significant, particularly in the parameter  $q$  of Eq. (3) and to depend largely upon the ratio of  $2k_F$  to  $K_p$ , where  $K_p$  is the wave vector of the first peak in  $S(Q)$ . In particular, when  $2k_F$  is close to  $K_p$  the thermopower increases slower than linearly with temperature, whereas when  $2k_F$  is larger than  $K_p$  the increase is faster than linear. These two extreme types of variation with temperature corre-

spond to the present calculation of  $2k_F/K_p \lesssim 1.04$ , a value which is probably very sensitive to the details of the structure factor.

## II. DETAILS OF THE CALCULATION

Including the temperature dependence of  $S(Q)$ , as pointed out by Cote and Meisel,<sup>13</sup> is not just a matter of using the experimentally available x-ray or neutron structure factors. Rather, the correct  $S(Q)$  is a particular average over the dynamic structure factor, which must be obtained by model calculations. In the present paper we follow the procedure described by Cote and Meisel,<sup>13</sup> using as a starting point the Fourier transform of the pair-distribution for a random close-packed cluster of 1000 atoms constructed by a Bennet algorithm on a computer.<sup>14</sup> The length scale was determined by choosing the hard-sphere diameter to be 2.54 Å for Zn and 3.12 Å for Mg, and the temperature scale by taking the Debye temperature as  $\Theta_D = 295$  K, appropriate to the Mg-Zn amorphous alloys.<sup>15</sup> In the calculations of  $q$  the potentials  $V(Q)$  were taken from Ashcroft and Langreth,<sup>16</sup> and values of  $r$  were chosen following the procedure of Ashcroft.<sup>17</sup> In the first instance, we attempted to calculate the temperature dependence of the thermopower of hypothetical amorphous Zn. In the absence of data, we chose to fit instead to values of liquid Zn,<sup>1</sup> using a value  $k_F = 1.65 \text{ \AA}^{-1}$  ( $E_F \sim 10.36$  eV), which gives a ratio  $2k_F/K_p = 1.11$ . This value is higher than that from a free-electron value for  $k_F$  and the experimental structure factor<sup>15</sup> (1.03). It corresponds to values of  $q$  and  $r$  of 1.35 and 0.03, respectively, at 300 K, and gives pronounced upward curvature to the temperature dependence, with a negative thermopower for hypothetical "amorphous zinc" below 450 K, as shown in Fig. 1.

To analyze the alloys we first identified the param-

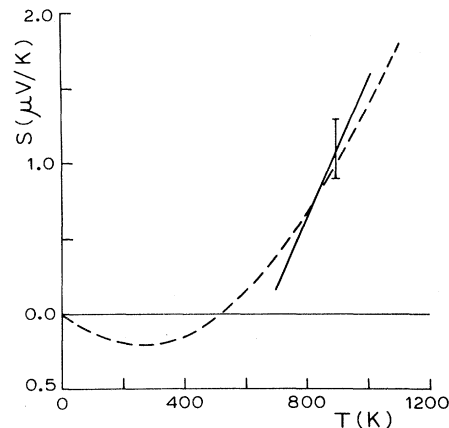


FIG. 1. Temperature dependence of the thermopower of hypothetical amorphous zinc. Dashed line, theoretical curve as discussed in the text. Solid line, data for liquid Zn from Ref. 1, with error bars.

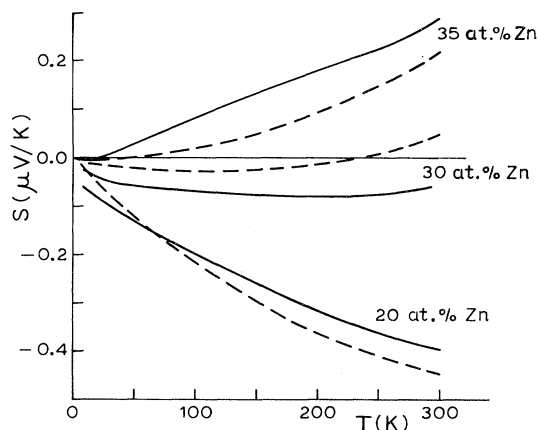


FIG. 2. Temperature dependence of the thermopower of amorphous Mg-Zn alloys. Solid lines, data from Ref. 4. Error bars are very small, but concentration values can be inaccurate to within  $\pm 1\%$ . Dashed lines, theoretical curves as discussed in the text.

eter  $\xi_2$  with this calculated thermopower for Zn. In principle, we would have preferred to calculate  $\xi_1$ , for Mg, in a similar fashion, but data for the liquid exist only at the melting point,<sup>1</sup> and in view of this we chose the parameter  $\xi_1$  to give the best fit to the alloy data. The value chosen was consistent with  $2k_F/K_p = 1.10$  and gives  $\xi_1 = 2.73$  at 300 K, a value which corresponds with the analysis of Baibich *et al.*<sup>4</sup>

Analysis of the alloys then proceeded by choosing a temperature-independent value of  $I$  [Eq. (6)] which gave a good fit to the concentration dependence at 300 K. Over the available range of concentration the dependence is approximately linear,<sup>4</sup> but the inclusion of  $I$  gives a characteristic parabolic shape to the (experimentally inaccessible) region at higher zinc concentration. The calculations were performed with experimental values for the resistivities  $\rho_1$ ,  $\rho_2$ , and  $\rho$  taken, respectively, from the liquid state [27.0 and 37.0  $\Omega$  cm (Ref. 9)] and from the alloy data.<sup>4</sup>

Temperature dependences of the thermopowers at different concentrations are displayed in Fig. 2. Agreement with the experimental curves is seen to be very good.

### III. DISCUSSION

The most significant feature of the calculations presented in this paper is that the Ziman expression for the thermopower is capable of describing nonlinear temperature dependence. The crucial parameter is seen to be the ratio of  $2k_F$  to  $K_p$  which determines the temperature dependence through the parameter  $q$ . The present results, using an artificial structure factor obtained from a hard-sphere packing, cannot be expected to give realistic values for the ratio which best fits the data, but nevertheless they give an excellent indication of qualitative trends. A

more realistic structure factor (perhaps derived from a relaxed structural model) would be expected to have a narrower first peak, so that fits to the data would be expected for slightly smaller values of the ratio. This would improve the agreement with the free-electron value mentioned in the text. Investigations in this direction are continuing.

It is also interesting to note that the temperature dependence of the thermopower of our hypothetical amorphous Zn reproduces rather well that of liquid Zn. Although the calculational techniques used for the temperature dependence of liquid thermopowers are rather different from those used in this paper<sup>9</sup> we believe that it would be fruitful to pursue the present approach using first-principles values of  $q$  and  $r$ .<sup>12</sup> Parallel calculations for liquid Hg and Tl would also be useful. In general, it becomes interesting to speculate on the reason for the *linearity* exhibited by the majority of liquid metals.<sup>1</sup> From our point of view, the temperature dependence of  $q$  is either absent (with  $2k_F$  far from  $K_p$ ) or, in these metals, confined to temperatures below the melting point.

The alloy calculations are interesting in that the trends with concentration are clearly reproduced even with the drastic approximations employed to minimize the number of free parameters. Individual fits to individual alloys can be obtained which are much superior to those shown in Fig. 2, but we chose instead to describe the alloys as a group. The key parameter is then the  $I$  occurring in Eq. (6). In principle this parameter could be calculated from the potentials and the structure factor, but in practice such a complex calculation would be exceedingly unreliable, although it might yield qualitative information about the temperature and  $k_F$  dependence of  $I$ . The other approximation, namely that all the partial structure factors are identical, is certainly very reasonable for the isoelectronic Mg-Zn alloys, and improvements are not likely to be significant.

In conclusion, we have shown that nonlinear temperature dependence of the thermopower in metallic glasses can be explained within the Ziman model. Dependence of the type exhibited by Mg-Zn alloys and by many Metglasses arises in a natural way. However, the low-temperature knee observed in several other metallic glasses<sup>3</sup> does not emerge from the calculations. An explanation of this effect must await further theoretical work.

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- \*Permanent address: Department of Physics, Karnatak University, Dharwad, 58003 India.
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