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# Comments on the Correlation between Parameters for Melting and Diffusion and on the Relaxion Mechanism\*

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This paper points out that the correlation between parameters for diffusion and melting is rather less accurate than the experimental data and that it fails to predict some interesting effects. It also shows that the "relaxion" model, which is based on the melting-diffusion correlation, cannot explain experimental results on the mass effect in diffusion.

Sherby *et al.*<sup>1</sup> recently pointed out a correlation between the activation volume for self-diffusion and melting and crystal structure parameters. Their paper is the latest of a series of papers, by different authors,<sup>2-10</sup> connecting diffusion to melting, and dating back at least to 1924, when Braune<sup>10</sup> compared the critical amplitude needed for a diffusional jump with the critical vibrational amplitude needed for melting in the Lindemann theory.<sup>11</sup> In the present paper, we first point out that the correlation between parameters for diffusion and for melting is in several cases a very poor approximation. Second, we criticize in detail a model proposed to explain the correlation between diffusion and melting, the "relaxion," proposed by Nachtrieb and Handler.<sup>2</sup>

The fact that the correlations between  $T_m$ , the melting temperature,  $L_m$ , the latent heat of melting, or  $L_s$ , the heat of sublimation, and  $Q$ , the activation energy for self-diffusion, are good only to about 10% has been noted by Birchenall<sup>12</sup> and Hoffman *et al.*<sup>13</sup> As values of  $Q$  are reproducible to  $\pm 2\%$  between laboratories,<sup>14</sup> it can be seen that the correlations are indeed imprecise. However, recent data indicate even more serious failures.

First, the correlation is based on the assumption that all plots of  $\log D$  vs  $1/T$  are straight lines; it thus ignores the curved Arrhenius plots found for self-diffusion in  $\beta$ -Ti,<sup>15</sup>  $\beta$ -Zr,<sup>16</sup> V,<sup>17</sup> Na,<sup>18</sup> and K.<sup>19</sup> Second, the activation energies for self-diffusion in  $\gamma$ -U<sup>20</sup> and  $\beta$ -Hf<sup>21</sup> estimated from correlation with  $T_m$  are a factor of 2 too high. Third, the correlation does not work even for the noble metals, whose diffusion properties are the most studied and the best understood. The correlation with  $T_m$  or  $L_m$  predicts  $Q_{Cu} \cong Q_{Au} > Q_{Ag}$ , but the data show  $Q_{Cu} > Q_{Ag} > Q_{Au}$  (Table I). Evidently, either correlation of  $Q$  with  $T_m$  or  $L_m$  will give a good order-of-magnitude estimate of  $D$ ; on the other hand, we are not inclined to have much faith in an atomic theory of diffusion constructed on the basis of a correlation that gives the wrong trend for the activation energies. Further, there are many other interesting and experimentally well-established diffusion phenomena, such as anisotropy in noncubic crystals, the systematic variation of activation energies for impurity diffusion with the position of the impurity in the Periodic Table, mass effects, ultrafast diffusion,<sup>22</sup> etc., which are not predicted by correlations with melting parameters. It is thus hard to see how these correlations can enhance our knowledge of diffusion on the atomic scale.

The one atomic model of diffusion inspired by the correlation between melting and diffusion is the relaxion model of Nachtrieb and Handler.<sup>2</sup> This model in effect says that the defect responsible for diffusion is a vacancy around which the nearest neighbors have relaxed to the extent that they form a liquid region 12–14 atoms in size. This model was in good accord with the data

available when it was published, and the relaxed vacancy is still almost universally considered to be the defect responsible for self-diffusion, at least in close-packed structures. We disagree only with the parts of the model that specify that the relaxion is such as to produce a region of liquid, and with the splitting up of the activation energy for self-diffusion on this basis. We also find it difficult to reconcile the results of experiments on the isotope effect in diffusion with the relaxion mechanism, as pointed out by Lazarus and Nachtrieb.<sup>23</sup>

The original relaxion model was based on the relation  $Q = 16.5 L_m$ . Of this, 12–14  $L_m$  was assigned to the relaxion formation energy  $H_f$ , leaving 2.5–4.5  $L_m$  for the motion energy  $H_m$ , giving, for fcc metals,  $(H_m/H_f)_{\max} = 0.375$ . However, experimental measurements on the quenching in of vacancies,<sup>24</sup> all published after original paper of Nachtrieb and Handler, yield a minimum value of  $H_m/H_f = 0.75$ . Thus the original relaxion model disagrees severely with well-established experimental data.

Estimation of the isotope effect for diffusion by the motion of a relaxion is made difficult by the vague description of the atom movements in a relaxion. On the motion of a relaxion, Nachtrieb and Handler say: "The process may be likened to "melting" and "freezing" one or two atoms at a time with an activation energy of the order of  $L_m$ . Since the activation energy for diffusion in monatomic liquids is of comparable magnitude, we think it likely that the cooperative movement of atoms within a relaxion is a process of similar probability." This quotation from Nachtrieb and Handler's paper does not make clear how many atoms undergo a diffusive displacement when the center of the relaxion moves one atomic spacing; the sentence on relaxion motion in the paper of Sherby *et al.*<sup>1</sup> is no help either. But this is a very important point because experimental results on the isotope effect for self-diffusion in close-packed metals show that one and only one atom undergoes a diffusive (permanent) displacement during one jump of the defect responsible for diffusion. To us, this experi-

TABLE I. Activation energy for self-diffusion in the noble metals (in kcal/mole).

Metal	Experimental value	16.5 $L_m$ <sup>a</sup>	18 $T_m \times R$ <sup>b</sup>
Cu	50.5 $\pm$ 0.2 <sup>c</sup>	51.15	47.96
Ag	44.3 $\pm$ 0.1 <sup>d</sup>	44.38	43.65
Au	42.26 $\pm$ 0.05 <sup>e</sup>	50.32	47.25

<sup>a</sup> Formula for  $Q$ , from Ref. 2.

<sup>b</sup> Formula for  $Q$ , from Ref. 3.

<sup>c</sup> S. J. Rothman and N. L. Peterson, Phys. Status Solidi 35, 305 (1969).

<sup>d</sup> Calculated from the data of C. T. Tomizuka and E. Sonder, Phys. Rev. 103, 1182 (1956).

<sup>e</sup> H. M. Gilder and D. Lazarus, Ref. 14.

mental fact is much better explained by the jump of a discrete vacancy than by adjusting the melting, freezing, and cooperative motion involved in the motion of a relaxation to give just one atomic displacement. In fact, except for the correlation of  $Q$  with  $L_m$ , we cannot think of any experimental data which are not explained at least as well as on the basis of a discrete vacancy (relaxed), as on the basis of a "relaxion".

Our last objection to the relaxion is its use by Sherby *et al.* to explain negative activation volumes. We find this rather unlikely for the following reason.<sup>25</sup> Since for most metals  $Q_F \geq Q_M$ , by Eqs. (19) and (20) of Sherby *et al.*  $\Delta V_F \geq \Delta V_M$ , so that to have  $\Delta V_D \geq 0$ ,  $\Delta V_F$  must be less than zero. Now, since the process of vacancy formation consists of removing an atom from the lattice and placing it on the surface ( $\Delta V = +\Omega$ ), and then letting the atoms around the vacancy relax, the  $\Delta V$  associated with the relaxion must be negative and greater in absolute value than the atomic volume  $\Omega$ , i.e., more atoms must be squeezed into the same place than were there before the vacancy was created. But if there are more atoms present in the same space than there were before the defect was created, the defect is an interstitial. Thus  $\Delta V_F < 0$  is difficult to accept for a relaxion, which, after all, is a vacancy. We also cannot envisage a diffusional jump that does not dilate the lattice, so  $\Delta V_M$  must also be positive.<sup>26</sup> Therefore negative volumes of activation could better be interpreted on the basis of an interstitial mechanism. This is just the interpretation given by Calais<sup>27</sup> to the negative  $\Delta V_D$  for  $\epsilon$ -Pu,<sup>28</sup> and has also been suggested by Haas<sup>29</sup> and Onsager and Runnels<sup>30</sup> for molecular diffusion in ice, the two cases of negative  $\Delta V$  cited by Sherby *et al.*

Thus we see that the correlation between diffusion and melting describes, within rather broad limits of error, only a limited class of diffusional phenomena. All the rest, which do not fit the correlation at all, include, in our view, the major unexplained experimental observations of diffusion in the solid state, such as the "anomalous" bcc metals, or ultrafast diffusion. A start on explaining these phenomena has been made on the basis of more atomistic theories of diffusion,<sup>18,31</sup> which have suggested experiments and theoretical analyses. If the "melting theory" is to be useful at this level, it will have to undergo radical alterations.

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<sup>1</sup>O.D. Sherby, T.L. Robbins, and A. Goldberg, *J. Appl. Phys.* **41**, 3961 (1970).

<sup>2</sup>N.H. Nachtrieb and G.S. Handler, *Acta Met.* **2**, 797 (1954).

<sup>3</sup>O.D. Sherby and M.T. Simnad, *Trans. Am. Soc. Metals* **54**, 227 (1961).

<sup>4</sup>V.I. Meshkov, *Izvestiya VUZ Chernaya Metalurgiya* No. 5, 93 (1960).

<sup>5</sup>K. Mukherjee, *Phil. Mag.* **12**, 915 (1965).

<sup>6</sup>K. Mukherjee, *Trans. AIME* **236**, 1324 (1966).

<sup>7</sup>W. Lange, *Z. Metallk.* **57**, 653 (1966).

<sup>8</sup>G.M. Neumann, *Z. Physik. Chem. (Frankfurt)* **56**, 342 (1967).

<sup>9</sup>J.A.M. van Liempt, *Z. Anorg. Allgem. Chem.* **195**, 366 (1931), quoted in W. Seith, *Diffusion in Metallen* (Springer, Berlin, 1955), p. 89.

<sup>10</sup>H. Braune, *Z. Physik. Chem. (Frankfurt)* **110**, 147 (1924), see Seith (Ref. 9).

<sup>11</sup>F. Lindemann, *Z. Physik* **11**, 609 (1910).

<sup>12</sup>C.E. Birchenall, in *Atom Movements* (American Society of Metals, Cleveland, 1951), p. 119.

<sup>13</sup>R.E. Hoffman, F.W. Pikus, and R.A. Ward, *Trans. AIME* **206**, 483 (1956).

<sup>14</sup>For example, for gold,  $Q = 42.26$  kcal/mole [H.M. Gilder and D. Lazarus, *J. Phys. Chem. Solids* **26**, 2081 (1965)], or  $Q = 41.65$  kcal/mole [S.M. Makin, A.H. Rowe, and A.D. LeClaire, *Proc. Phys. Soc. (London)* **70**, 545 (1957)].

<sup>15</sup>J.F. Murdock, T.S. Lundy, and E.E. Stansbury, *Acta Met.* **12**, 1033 (1964).

<sup>16</sup>J.I. Federer and T.S. Lundy, *Trans. AIME* **227**, 592 (1963).

<sup>17</sup>R.F. Peart, *J. Phys. Chem. Solids* **26**, 1853 (1965).

<sup>18</sup>J.N. Mundy, *Phys. Rev. B* **3**, 2431 (1971).

<sup>19</sup>J.N. Mundy, R.J. Porte, and T. Miller, *Phys. Rev. B* **3**, 2445 (1971).

<sup>20</sup>S.J. Rothman, L.T. Lloyd, and A.L. Harkness, *Trans. AIME* **218**, 605 (1960).

<sup>21</sup>F.R. Winslow and T.S. Lundy, *Trans. AIME* **233**, 1790 (1965).

<sup>22</sup>For a review, see N.L. Peterson in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1968), Vol. 22, p. 409 ff.

<sup>23</sup>D. Lazarus and N.H. Nachtrieb, in *Solids under Pressure*, edited by W. Paul and D.M. Warschauer (McGraw-Hill, New York, 1963), p. 44.

<sup>24</sup>For a table of values and references to the original literature, see Ref. 22, p. 415.

<sup>25</sup>This argument was suggested by N.L. Peterson.

<sup>26</sup>Reference 23, p. 60.

<sup>27</sup>D. Calais (private communication).

<sup>28</sup>J.A. Cornet, thesis (Orsay University, 1970) (unpublished). This is the only metallic system for which  $D$  increases monotonically with  $P$ . Previous results that gave negative values of  $\Delta V_D$  at low pressures, obtained on polycrystalline samples of two metals which are similar to  $\epsilon$ -Pu except that their density decreases on melting, are anomalous. The self-diffusion coefficient of  $\gamma$ -U [M. Beyeler and Y. Adda, in *Physics of Solids at High Pressures*, edited by C.T. Tomizuka and R.M. Emerick (Academic, New York, 1965), p. 349] and the diffusion coefficient of Fe in  $\beta$ -Ti [R.F. Peart, *Phys. Status Solidi* **20**, 545 (1967)] increase with  $P$  at low  $P$ , go through a maximum, and decrease. However, a recent measurement on the effect of pressure on self-diffusion in  $\beta$ -Ti [R.N. Jeffery, thesis (University of Illinois, 1970) (unpublished)] indicates normal behavior with  $\Delta V_D > 0$ . An anomalous peak in the  $\ln D$ - $P$  curves was also found for polycrystalline silver, although single-crystal samples showed normal behavior (Beyeler and Adda *loc. cit.*).

<sup>29</sup>C. Haas, *Phys. Letters* **3**, 126 (1962).

<sup>30</sup>L. Onsager and L.K. Runnels, *Proc. Natl. Acad. Sci. U.S.A.* **50**, 208 (1963).

<sup>31</sup>J.W. Miller, *Phys. Rev. B* **2**, 1627 (1970).