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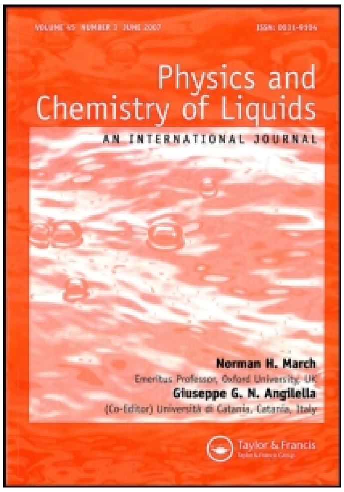

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Self-diffusion of Tin in a Liquid Tin-Lead Alloy at the Eutectic Composition

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By the shear cell technique, the self-diffusion coefficient of tin in a liquid Sn-38.1 wt% Pb alloy has been measured in the temperature range from 466°K to 786°K. The variation of $D^{Sn^*}_{Sn\text{-}38.1\,wt\%Pb}$ with temperature doesn't follow the Arrhenius type equation and shows a change in its slope about 573°K. A qualitative explanation of this behaviour is attempted based on either a cluster hypothesis or rigid sphere liquid model.

1 INTRODUCTION

Measurements of viscosity coefficient, as a function of temperature,[1,2] in liquid Sn-38.1 wt% Pb (eutectic composition), show a gentle change in slope near 623°K.

Taking into account Ubbelhode's theory,[3] R. Kumar[4] explains that this behaviour is due to the presence of clusters (pseudo-molecules) in the liquid, though this interpretation is still an open question.

The aim of this work is to verify if a similar change could be seen in self-diffusion measurements, and in that case to discuss why it arises.

2 EXPERIMENTAL METHOD

The experimental technique employed in this work was the shear cell, which had been first used by N. H. Nachtrieb for liquid metals (Hg.Ga).[5,6]

The shear cell was made in graphite, which avoids bubble gas formation and chemical reaction with this liquid alloy. Furthermore, graphite is very easy to handle. The cell consisted of ten disks, mounted coaxially; each one was 0,5 cm. thick, with three off center capillary holes of 1 mm. diameter each.

Before a diffusion experiment, capillaries of the two last disks – which contained the Sn radiotracer – were misaligned with respect to the others (Fig. 1B), until the run began by aligning the holes (Fig. 1C). The experiment was finished by rotating each disk in order to section the liquid thread. The measurement of the specific activity in each capillary section allowed us to obtain the diffusion profile.

Fick's equation solution with boundary conditions:

$$t = 0 \quad \left\{ \begin{array}{l} c = c_0 \; 0 < x < h \\ c = 0 \; h < x < L \end{array} \right. \qquad t \neq 0 \quad \left\{ \left(\frac{\partial c}{\partial x}\right)_{x=0} = \left(\frac{\partial c}{\partial x}\right)_{x=L} = 0 \right.$$

is[7]

$$c(x,t) = \frac{c_0 h}{L} + \sum_{n=1}^{\infty} \frac{2c_0}{3\pi} \operatorname{Sen}\left(\frac{n\pi h}{L}\right) \operatorname{Cos}\left(\frac{n\pi x}{L}\right) \exp\left[-\frac{\pi^2 n^2 Dt}{L^2}\right]$$

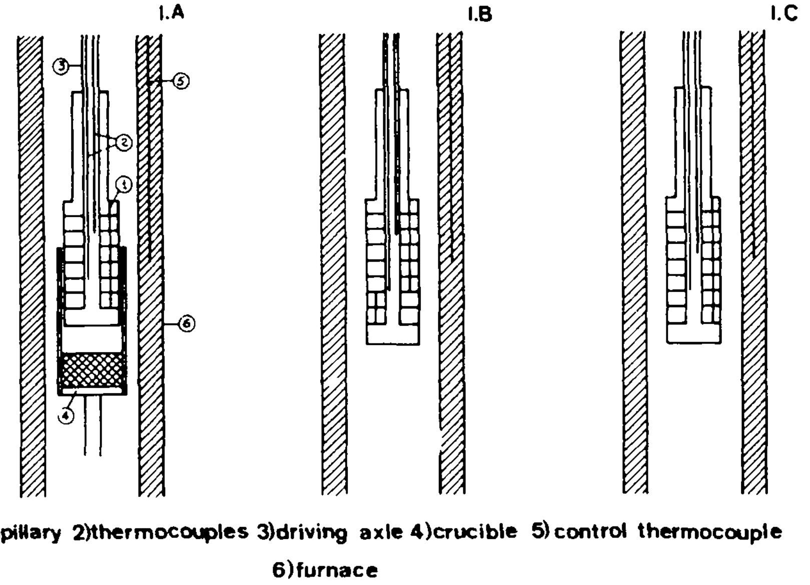

FIGURE 1A Diagram shows capillary filling.
FIGURE 1B Diagram shows the shear cell before the diffusion run.
FIGURE 1C Diagram shows the shear cell during the diffusion run.

where:

c_0 = initial capillary concentration; t = diffusion time.
h = thickness of the disks where the radiotracer is initially (t = 0).
L = capillary length.

In our case h = 1.0 cm, L = 5.0 cm.

A numerical solution of this problem can be found in the Stefan-Kawalki Tables.[8]

All the operations were performed under Argon pressure (~ 1 Kg), with a previous de-gassing under 10^{-4} mm Hg. The temperature was controlled with a P.I.D. thermoregulator and measured with chromel-alumel thermocouples. A small positive temperature gradient ($\leq 0.2\,^\circ$C/cm) avoided convective effects – thermodiffusion was considered negligible.

The radiotracer was ${}_{50}\mathrm{Sn}^{113}$, with a half-life of 112 days. Tin and lead were 4N purity.

The filling of the capillaries was achieved by plunging either the lower disks in a Sn-38.1 wt% Pb liquid alloy (with a dilute proportion of Sn^{113}) or the upper disks in an ordinary isotopic composition liquid alloy (Fig. 1A). Before the disks were sunk, they were immersed in the liquid; pressurised Argon gas (2–3 Kg) was admitted in the furnace to force the liquid to enter the capillaries.

3 EXPERIMENTAL RESULTS

While the shear cell technique has the major advantage of allowing the cutting of the liquid column, a stirring may occur when the disks are rotated to stop the experiment.[9] It seems probable that the larger the ratio between the width of each disk and the capillary hole diameter is, the less is the mixing which would occur. As a matter of fact, we have never obtained the same value of the self-diffusion coefficient in the three capillaries for each experiment.

Experimental values, having a σ (mean square deviation)/D_{average} ratio larger than 10% were not considered. As is shown in Figure 2 a slope change is observed near ~ 573 °K. This is not strictly in agreement with the observed values of viscosity coefficient (Figure 3), which indicates a change near 593 °K[1] or 673 °K.[2] Actually, the dispersion in the experimental points prevents us determining where the "exact" temperature points of inflection is. At any rate, it is evident that there is not a drastic slope change, as in some other liquids i.e. Te.[10] The results are shown in Table 1.

In Figure 4, a plot of Ln $D^{\mathrm{Sn}^*}_{\mathrm{Sn\text{-}38.1\,wt\%\,Pb}}$ versus 1/T is shown. An adjustment by the least squares method gives the following values for the pre-exponential

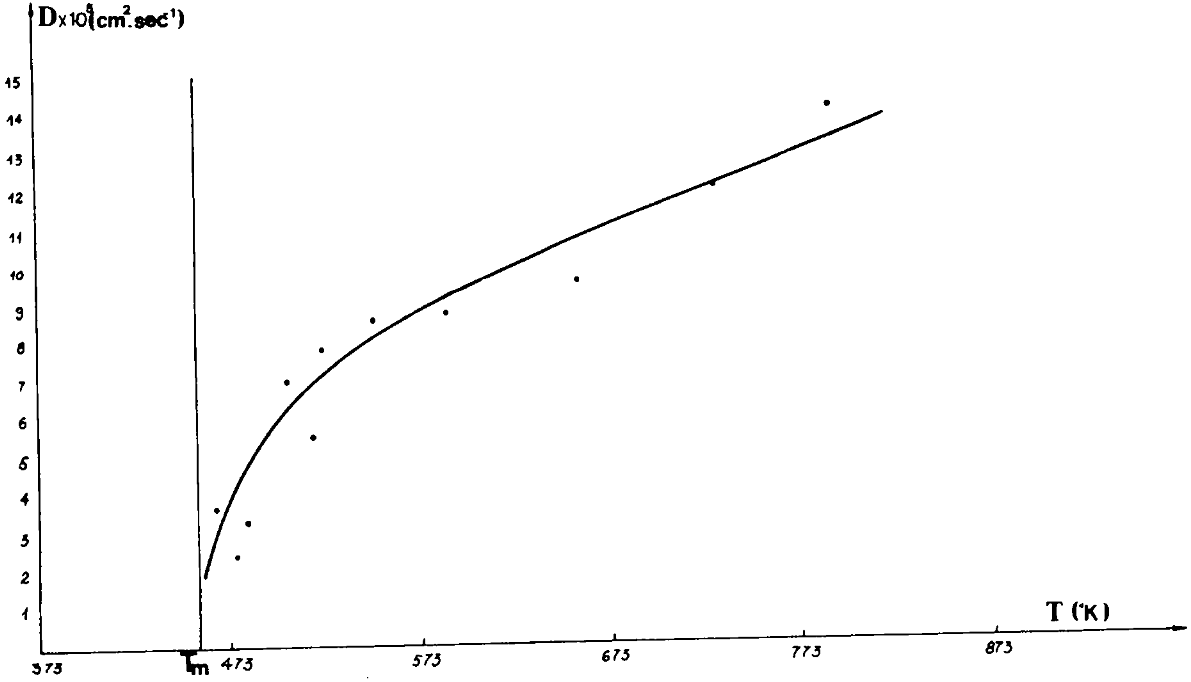

FIGURE 2 Self-diffusion coefficient of tin in the liquid Sn–Pb eutectic alloy as a function of the absolute temperature.

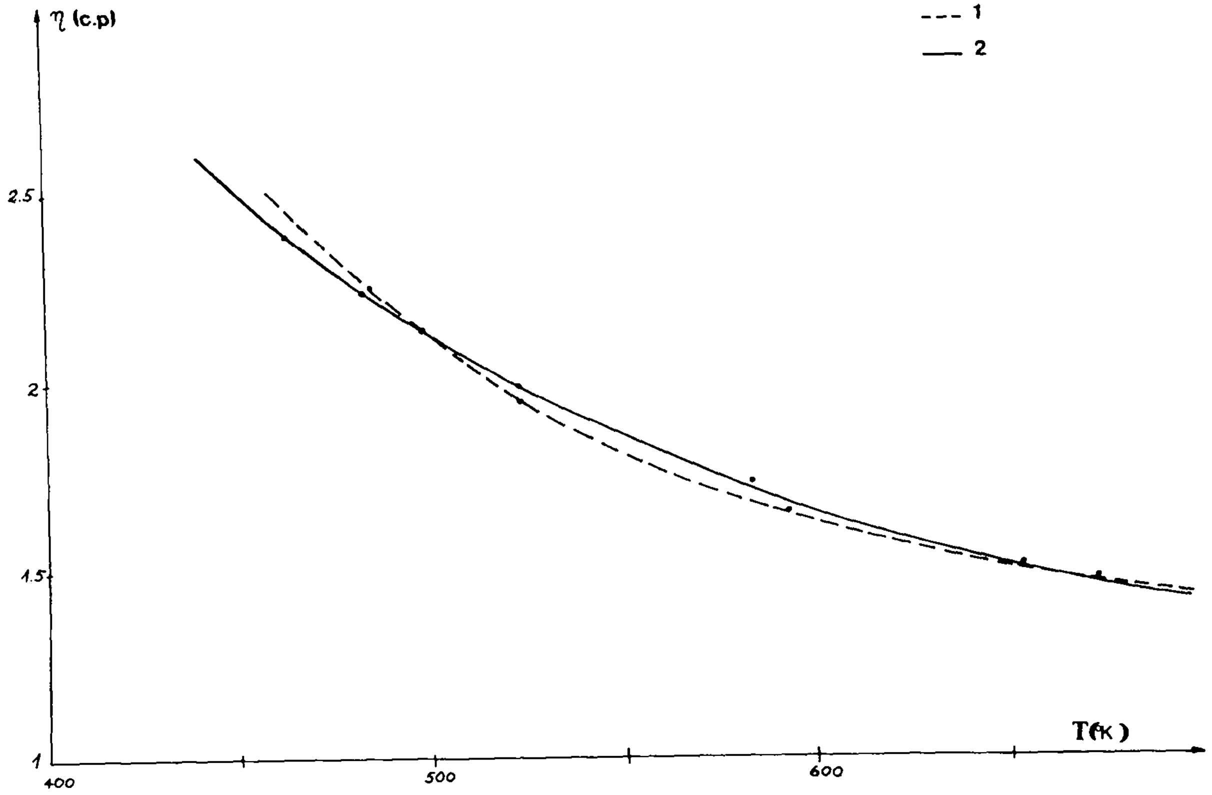

FIGURE 3 Viscosity of liquid Sn–Pb eutectic alloy.
1. J. Fisher and A. Phillips.
2. M. Shiraishi *et al.*

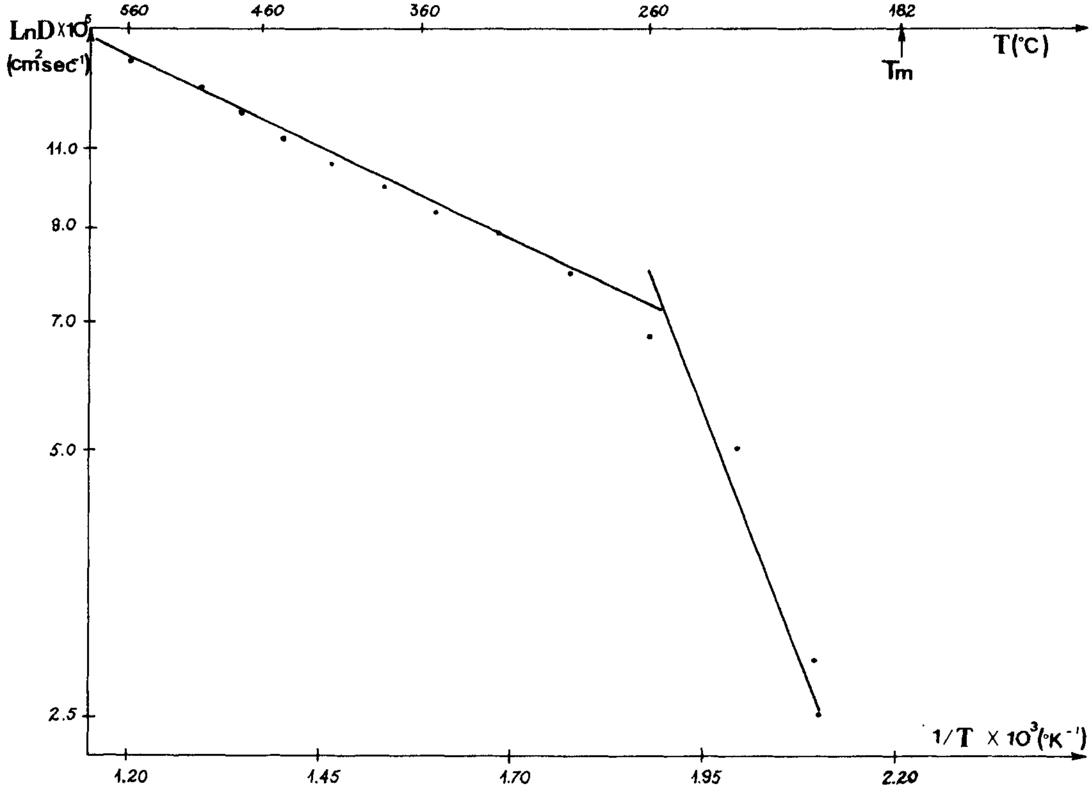

FIGURE 4 Ln D vs 1/T plot for the self-diffusion coefficient of tin in liquid Sn–Pb eutectic alloy.

TABLE 1

Self-diffusion coefficient of Sn^{113} in the molten Sn–Pb eutectic alloy.

$D.10^5(cm^2\text{-}sec^{-1})$	T(°K)	t(sec)
3.6	466	21,600
2.4	477	16,200
3.3	482	19,800
2.6	488	16,200
7.0	503	9,600
6.6	516	16,200
7.8	521	16,200
8.5	548	10,800
8.8	586	14,400
6.9	604	10,800
9.5	656	9,000
12.1	728	9,000
14.0	786	9,000

term and the activation energy.

$$\begin{cases} D_{O1} = 2.67\ cm^2\text{-}sec^{-1} \\ Q_1 = 10.55\ k\text{-}cal.mole^{-1} \end{cases} \qquad T_m < T < 573\,°K$$

$$\begin{cases} D_{O2} = 6.88.10^{-4}\ cm^2\text{-}sec^{-1} \\ Q_2 = 2.47\ k\text{-}cal.mole^{-1} \end{cases} \qquad 573\,°K < T < 786\,°K$$

As it can be easily seen, $D^{Sn^*}_{Sn-38.1\,wt\%\,Pb}$ does not follow an Arrhenius law in all the temperature domain. This result is not in agreement with the observed value of viscosity.[2]

4 DISCUSSION

By using different experimental techniques several authors have suggested the presence of clusters in this liquid alloy. A. Lashko and A. V. Romanova,[11] performed X-Rays diffraction experiments and they claimed that they had found-between 473 °K and 673 °K – a structure which consists in domains in which one of the components is preferentially concentrated ("quasi-eutectic structure"). This structure was not observed above 673 °K.

R. Kumar,[3] has used a centrifuging technique, and he came to the following results:

The clusters of lead and tin are approximately 35Å and 25Å respectively.
The size of each cluster is increased with temperature (up to ~973 °K).
The calculated heat of formation of each cluster has a value of 25 k-cal.mole⁻¹ (at 523 °K).

He applied Einstein's equation

$$\frac{\eta_i}{\eta_{si}} = 1 + 2.5\,\phi + 7\,\phi^2 + \ldots$$

where:

η_i = actual value of viscosity.

η_{si} = value that the viscosity would have if none of the molecules were grouped in clusters.

ϕ = volume fraction of suspended particles.

The calculated results are:

$$0.9 > \phi > 0.01 \text{ for } 485\,^\circ\text{K} < T < 673\,^\circ\text{K}$$

$$\phi \rightarrow 0 \text{ for } T > 673\,^\circ\text{K}.$$

This is a far from rigorous treatment of the problem – in spite of being commonly used – because to consider clusters as rigid spheres is an evident oversimplification. The lifetime of a cluster, though much larger than the jump frequency is not infinite. It is interesting to point out that in his original paper Einstein used this theory in the case of a very dilute solution of sugar in water.[12] Of course, it is right to consider sugar molecules as rigid spheres of infinite lifetime, but this is not the case of clusters which are in a dynamical process of aggregation and dissociation. On the other hand, since the activity of tin and lead deviates positively from Raoult's law,[13] the atomic interaction between like atoms is larger than between unlike atoms. Taking into account the cluster hypothesis, we could explain, at least qualitatively, the different behaviour of $D^{Sn^*}_{Sn\text{-}38.1\,wt\%\,Pb}$ in two different domains of temperature. Between $T_{melting}$ and ~573 °K, relatively small changes in temperature produce dissociation of the clusters, and the diffusion flow is substantially increased. Above 573 °K the liquid is "monomeric" and the variation of the self-diffusion coefficient is less rough. As a matter of fact, the cluster hypothesis does not lead to a prediction of a numerical value for the diffusion coefficient.

It is well known that several different theoretical approaches have been used to give a quantitative description of the diffusive process in monoatomic liquids,[9] and increasingly mathematical complexity must be expected when the problem of binary liquid alloys is treated.

For example, H. J. Raveche and J. E. Mayer,[14] starting from a statistical-mechanical point of view, had developed a method for treating a liquid mixture away from thermodynamical equilibrium. Nevertheless, they arrived at equations – admittedly cumbersome – where D depends on pair potentials and the equilibrium pair and the equilibrium triplet correlation functions. The need to know this last function makes it extremely difficult to make a thorough test of this theory.

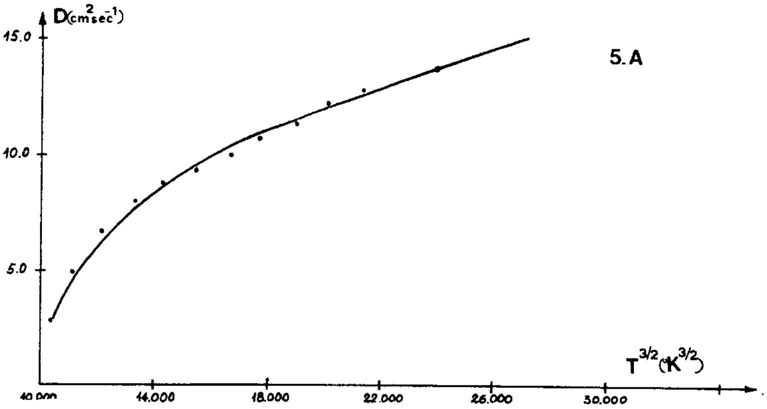

FIGURE 5A $D^{Sn^*}_{Sn\text{-}38.1wt\%Pb}$ versus $T^{3/2}$.

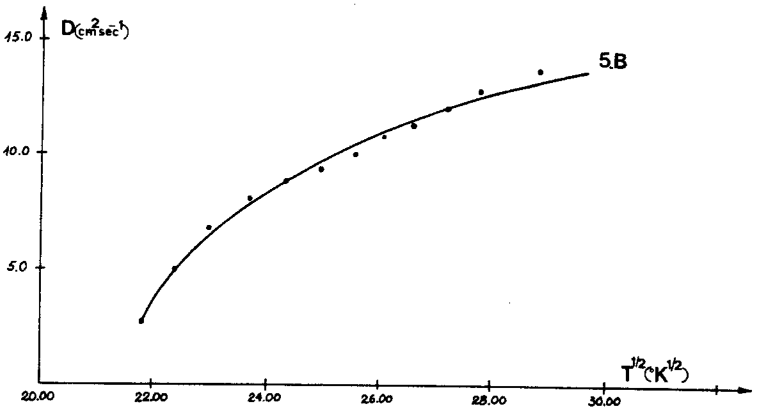

FIGURE 5B $D^{Sn^*}_{Sn\text{-}38.1wt\%Pb}$ versus $T^{1/2}$.

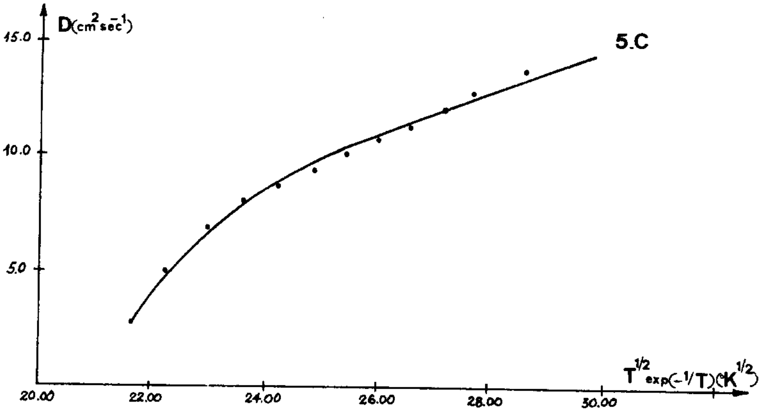

FIGURE 5C $D^{Sn^*}_{Sn\text{-}38.1wt\%Pb}$ versus $T^{1/2}\exp(-1/T)$.

D. Kessel, H. Witte and A. Weiss,[15] have developed the Cohen-Turnbull model in liquid mixtures. They suppose that each of the physical magnitudes involved in this theory, follow a simple additivity rule. As the resistivity[16] and the viscosity[2] also follows this rule, it is tempting to apply this approximation to our alloy. But it can be seen in Figure 5C that $D = f[T^{1/2}, \exp(-1/T)]$ does not show linearity. It could be argued that the hard-sphere diameter or the thermal expansion coefficient also changes with the temperature. Unfortunately, these two magnitudes are related by a straightforward relationship,[17] so any independent adjustment of each of them would seem rather improper. Theoretical models which predict other temperature dependences of D do not yield straight lines. (Figs. 5A and 5B).

At any rate, if one accepts the rigid sphere liquid model the change in the slope must be ascribed to a change in its diameter.

Summing up

Neither hypotheses – cluster or rigid sphere models – lead to a satisfactory quantitative explanation of the variation of D with the temperature.

Both hypotheses agree that the change in the slope is due to a change in the size of the elements which take part in the atomic motion.

Acknowledgments

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