

# Interstitialcy theory of simple condensed matter

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**Abstract.** A simple, more physical and compelling version of the Interstitialcy Theory of Simple Condensed Matter than that given previously is provided here. Also, computer simulation and direct and indirect experimental evidence is updated and reviewed. The theory is based on the properties of an interstitial in the interstitialcy, sometimes known as the dumbbell configuration. A free energy is derived, taking account of the unusually large shear susceptibility and vibrational entropy of the dumbbell to find the thermodynamic and kinetic properties of simple liquids and glasses. The connection between theory and experiment for some of the more notable properties of simple condensed matter found later is also discussed. The direct visual observation of interstitial diffusion to the surface in platinum near 20 K in irradiated thin films by Morgenstern et al. [M. Morgenstern, T. Michely, G. Comsa, Phys. Rev. Lett. **79**, 1305 (1997)] is found to be sufficient compelling evidence for the interstitialcy theory.

## 1 Introduction

We give here a simpler, more physical and compelling version of the Interstitialcy Theory of Simple Condensed Matter (ITCM) than that given previously. We are not aware of any other theory that gives the thermodynamic and kinetic properties of simple matter in terms of the properties of an intrinsic defect, known from earlier radiation damage studies. This is the interstitial in the interstitialcy configuration, sometimes referred to as the split or dumbbell configuration. It is found that many complex alloys have the same properties.

This theory was given previously [1], but in a form not easily understood, due primarily we believe, to a combination of terms made to meet a space available restriction, so that the physical effects were less easily recognized. The unusual properties of liquids and glasses found are due primarily to the large [1] shear susceptibility and [2] entropy arising for crystals containing a few interstitialcies. These, in turn, result from the basic static and dynamic properties of the dumbbells. They are calculated here quantitatively as simple derivatives of the free energy.

We show that the key quantity providing a second minimum in the free energy representing the liquid state at high enough temperatures is the vibrational entropy. It decreases at high concentration because of interactions between the interstitialcies which reduce the amplitude of vibration, and increase the vibrational frequencies, decreasing the entropy. This is what provides the second minimum representing the liquid state.

## 2 The Helmholtz free energy

The Helmholtz free energy  $A$  is given by:

$$A = U - TS, \quad (1)$$

where  $U$  is the internal energy,  $T$  the temperature and  $S$  the entropy. The Gibbs free energy is given by:

$$\mathcal{G} = A + pV.$$

$A$  is dependent on the independent variables: volume  $V$ , the shear strain  $\varepsilon$ , and temperature  $T$ , as well as the interstitialcy concentration  $c = n/N$ , where  $n$  is the number of interstitialcies in a mole  $N$  of molecules, and  $N$  is Avogadro's number.

$$A = A(V, \varepsilon, T : c) \quad \text{and} \quad \mathcal{G} = \mathcal{G}(p, \sigma, T : c), \quad (2)$$

where  $p$  is the external pressure and  $\sigma$  is an external shear stress. The shear dependence is essential to the theory and is usually ignored in other formulations.

We then have the thermodynamical properties

$$P = -\partial A / \partial V |_{T,c}, \quad \sigma = \partial A / \partial \varepsilon |_{V,c}, \quad \text{and} \quad S = -\partial A / \partial T |_{V,c} \quad (3)$$

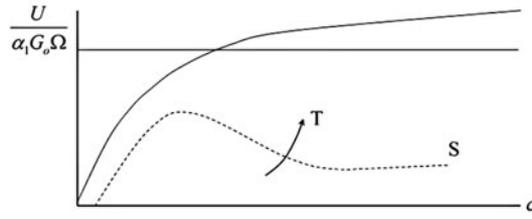
as first derivatives of  $A$  with

$$B = -V dP / dV = V \frac{\partial^2 A}{\partial V^2}, \quad G = \frac{\partial \sigma}{\partial \varepsilon} = \partial^2 A / \partial \varepsilon^2,$$

and

$$C_v = -T \partial S / \partial T = -T \frac{\partial^2 A}{\partial T^2} |_{V,\varepsilon} \quad (4)$$

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**Fig. 1.** The internal energy (solid line) and the entropy term (dashed line proportional to the temperature) as a function of the interstitial concentration.

as second derivatives, where  $B$  is the bulk modulus,  $G$  the shear modulus, and  $C_v$  is the specific heat at constant volume.

For a crystal, we take an ideal crystal as one which obeys the Murnaghan equation of state (1)  $B/B_0 = v^{-B^1} = 1 + B'(p/B_0)$ , valid to megabar pressures for most metals, where  $B$  depends only on volume,  $B = B(V, 0, 0)$ , and  $v = (V/V_0)$ .  $G$  depends on shear strain and temperature  $G = G(V, \varepsilon, T; c)$ , and is periodic for shear displacements in a crystal.  $B' = dB/dp$  is a dimensionless constant, with typical values near 5 for most metals, and 8 for noble gas crystals.

The internal energy  $U$  of a crystal containing a concentration  $c$  of interstitials must be expressible in terms of the macroscopic variables. By a dimensional analysis we find

$$\partial U / \partial c = \alpha_1 G \Omega + \alpha_2 B \Omega, \quad (5)$$

where  $\Omega$  is the volume per atom, and  $\alpha_1$  and  $\alpha_2$  are constants fitted to experimental results. It is expected (1) that  $\alpha_2 < \alpha_1 = 1 - \alpha_2$ . Earlier it was found (1) that the periodicity of the lattice implies

$$G/G_0 = \exp(-\beta c), \quad (6)$$

where  $\beta$  is a (large) shear susceptibility constant  $\sim 20$ .

Now,

$$U = \int_0^c [\alpha_1 G \Omega + \alpha_2 B \Omega] dc = \frac{\alpha_1 G_0 \Omega}{\beta} [1 - e^{-\beta c}] + \alpha_2 B \Omega c \quad (7)$$

a normalized internal energy is given by:

$$U / (\alpha_1 G \Omega_0) = [1 - \exp(-\beta c)] / \beta + (\alpha_2 / \alpha_1) (B_0 / G_0) c. \quad (8)$$

This is shown as the solid line in Figure 1.

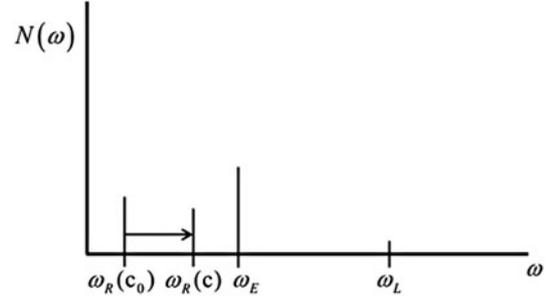
### 3 The entropy

The entropy is the sum of a configurational ( $S_c$ ) and a vibrational ( $S_v$ ) entropy,

$$S = S_c + S_v. \quad (9)$$

The configurational entropy per defect  $S_c/nk$  is

$$S_c/nk = [1 + \ln(z/c)], \quad (10)$$



**Fig. 2.** The Einstein frequency  $\omega_E$ , resonant frequency  $\omega_R$ , and local mode frequency  $\omega_L$  sketched schematically.  $\omega_R$  is a function of concentration  $c$ , while  $\omega_E$  and  $\omega_L$  are not.

where  $k$  is Boltzman's constant, and  $z$  is the number (3) of independent orientations of the interstitialcy. This differs only by the factor  $z$  from the more familiar expression for a vacancy.

Then

$$\Delta S_c / Nk = c [1 + \ln(z/c)]. \quad (11)$$

The vibrational entropy per defect can be much larger and is known from radiation damage studies done earlier [3]. Approximating the crystalline mode frequencies by an Einstein frequency  $\omega_E$ , the 5 resonant modes by a frequency  $\omega_R$ , and the 6 local modes by a frequency  $\omega_L$ , we have:

$$\frac{\Delta S_v}{Nk} = c \left\{ 5 \ln \frac{\omega_E}{\omega_R} + 6 \ln \frac{\omega_E}{\omega_L} \right\}. \quad (12)$$

The resonant mode frequencies are given by:

$$\frac{\omega_R(0)}{\omega_E} = \frac{L_E}{L_R} = \frac{1}{5.3}, \quad (13)$$

where  $\omega_R(0)$  is  $\omega_R$  at  $c = 0$ , and  $L$  is the width of the interstitialcy.

The resonant modes interact with each other at finite  $c$ . They intersect, decreasing the displacements and increasing the frequencies, as indicated in Figures 2 and 3.

$$N = n(0) + n(c),$$

so that

$$1/L_c = 1/L_R + \delta c, \quad (14)$$

or

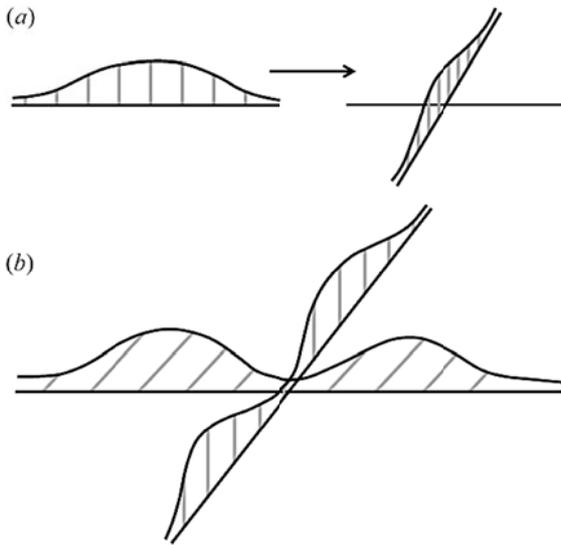
$$L_R/L_c = 1 + \delta L_R c, \quad (15)$$

where  $\delta$  measures the strength of the interaction. Then

$$\frac{\omega_c}{\omega_E} = \frac{L_E}{L(c)} = \frac{L_E}{L_R} \frac{L_R}{L(c)} = \frac{L_E}{L_R} (1 + \delta L_R c) = \frac{1}{5} (1 + \delta L_R c). \quad (16)$$

Now the total entropy change becomes

$$\begin{aligned} \frac{\Delta S}{Nk} &= \frac{\Delta S_c}{Nk} + \frac{\Delta S_v}{N\omega} \\ &= \left\{ 5 \ln 5.3 - 5 \ln (1 + \delta L_R c) + 6 \ln \frac{\omega_E}{\omega_L} + \left( 1 + \frac{\ln z}{c} \right) \right\}. \end{aligned} \quad (17)$$



**Fig. 3.** Two interacting interstitialcies (a) at low  $c$  and (b) at finite  $c$ . The scale is increased about a factor of two between (a) and (b).

The high frequency local modes  $\omega_L$  provide an approximately constant contribution  $6 \ln \frac{\omega_E}{\omega_L} = -3.29$ . This can be combined with the crystal constant term in  $\omega_R$

$$5 \ln 5.3 \text{ to give } 5(1.67) - 3.29 = 5.06.$$

Then  $\Delta S/Nk$  becomes:

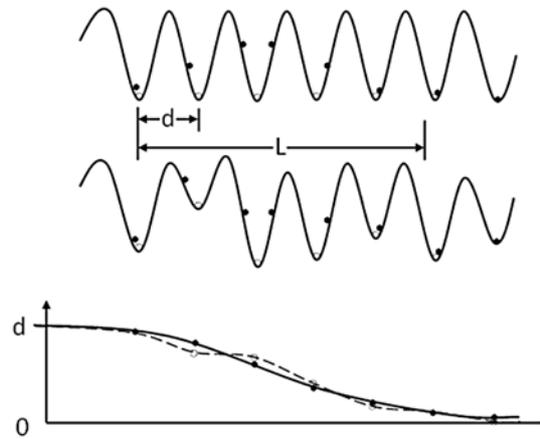
$$\frac{\Delta S}{Nk} = \{5.06 - 5 \ln(1 + \delta L_R c) + (1 + \ln zlc)\}. \quad (18)$$

The interaction term with  $\delta$  provides a negative contribution, decreasing the entropy as shown in Figure 1 (dashed line), and providing a second minimum in  $A$  for high enough temperatures. A fit to the Lindemann law [1,4] requires interaction strengths near  $\delta L_R = 0.8$ .

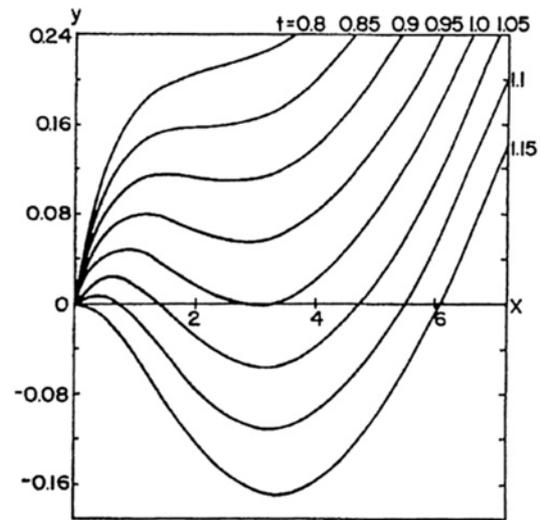
A representation of the interstitialcy is shown in Figure 4 for simple materials. For  $c = 0$ , all atoms are at equally spaced minima in a straight line. When an extra atom is forced in, the atoms are pushed into a Frenkel-Kontorova [2] solitonic configuration of width  $L$ . For an alloy, the displacements are changed slightly, but the topological pattern remains the same, so that complex materials often behave as simple materials, producing only a very small isotope effect.

As far as we are aware, it was Frenkel [3] who first used the term “condensed matter”, presumably to emphasize the close relationship between the crystalline and liquid state of matter. Frenkel recognized the necessity of an intrinsic defect, but was unaware of the later results [5–9] distinguishing the properties of vacancies and interstitials. He proceeded assuming the necessary defects were vacancies. His work was done in the 1920’s, but publication was delayed because of world war II.

Combining the enthalpy and entropy terms, one obtains the result for  $A(c)$  given in Figure 5 for different temperatures. This is essentially the same as that found

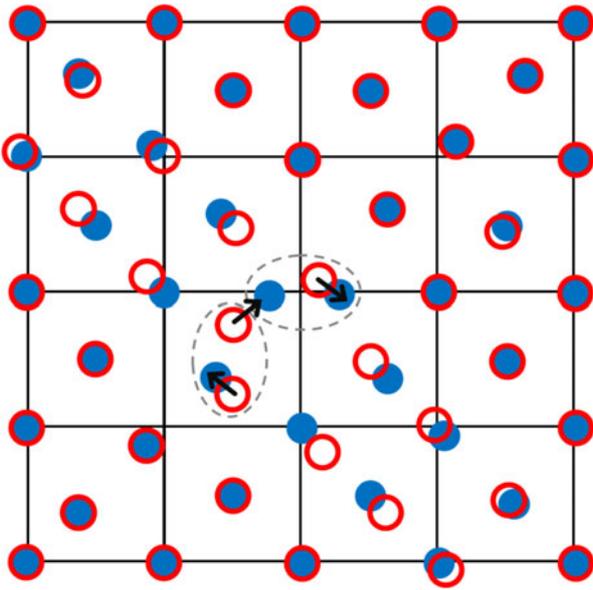


**Fig. 4.** Particle positions/displacements. An interstitial forced into the lattice produces displacements over a range  $L$  in a Frenkel-Kontorova pattern. The topological singularity is more important than the finite strain, so that complex materials often behave as simple materials, producing only a very small isotope effect.  $d$  is the average nearest-neighbor distance in the liquid or glassy state. Schematic indicates particle positions for crystalline state (open circles) and interstitialcy configurations (closed circles). Schematic indicates particle displacements from positions before interstitialcy insertion for crystalline state (solid circles) and glassy state (open circles and dashed line).



**Fig. 5.** The (normalized) Gibbs free-energy difference  $y$  as a function of the (normalized) interstitialcy concentration  $x$  for different temperatures  $t$ . The temperature is normalized to the melting temperature. The parameters are chosen for copper.

earlier [10], as the parameters are the same. For low  $T$ , there is only one minimum near  $c = 0$  for the solid state for all  $T$ . For high enough  $T$ , there is a second minimum at higher  $T$  representing the liquid state. When  $\Delta A$  and  $\partial \Delta A / \partial T$  are 0,  $T$  is the melting temperature  $T_m$  and  $c$  is  $c_m$ . This gives a new form of the Lindemann law of melting but has nothing to do with Lindemann’s critical average molecular displacement amplitude. At  $T_m$ ,



**Fig. 6.** Elementary jump of an interstitialcy in an fcc Lattice. Open circles (red), before jump; closed circles (blue), after jump.

the mean-square displacement amplitude is not uniformly distributed as assumed by Lindemann [4], but localized instead at the interstitialcies, as indicated in Figure 3. For high enough interstitialcy concentrations, they intersect, reducing the vibrational amplitude and entropy and providing the second minimum in  $A$  representing the liquid state.

At the inflection point of  $\Delta A(c)$ , known as the Kauzmann temperature  $T_k$ ,  $\Delta S = 0$ . For lower temperatures the entropy would become negative. Many theories have been invented to avoid this. Other properties would become unusual as well. For example, the liquid state shear modulus would be comparable to the bulk modulus. This does not occur in the ITCM model since this is not a quasi-equilibrium point and the system freezes into a frozen liquid (amorphous) state as the temperature is reduced, toward  $T_k$ .

For an interstitial jump, the changes in particles positions are as shown in Figure 6. The configuration (dashed lines) moves a nearest neighbor distance. However no particle moves more than a fraction of that. This is similar to the displacements for a dislocation in a crystal.

From equation (18), one sees that the net change in the free energy is a difference between two large terms. Physical properties given as derivatives are additional differences. The good agreement with experiment found [11–13] for these quantities implies that the free energy has been given by the model with very high accuracy.

## 4 Comparison with computer simulations, direct and indirect experiments

Using the shoving model put forward by Dyre et al. [14], the kinetic properties of simple matter are also brought

within the framework of the ITCM. The shear modulus is used to describe the migration energy of a particle. This is similar but somewhat different from the ITCM, for which the activation energy, also mainly proportional to  $G$ , represents the activation energy of diffusion, including the formation energy. The migration energy is too small for simple materials to cover the large observed range of viscosities and diffusion. There have been many review articles given by Dyre and his coworkers. One of the most recent and comprehensive is *The glass transition and elastic models of glass-forming liquids* [15].

A few selected experimental and theoretical characteristic features of the dumbbell will be mentioned here briefly.

### 4.1 Computer simulations

The extended nature involving many atoms of the interstitialcy was first seen by Schober [16] and his associates. The structure for simple metals is found in computer simulations by Kogure et al. [17,18] using the best available potentials. An interstitialcy jumping from the liquid onto the crystal surface was found by Ashkenazy and Averbach [19] and to the surface from the interior by Morgenstern et al. [20] (Fig. 8).

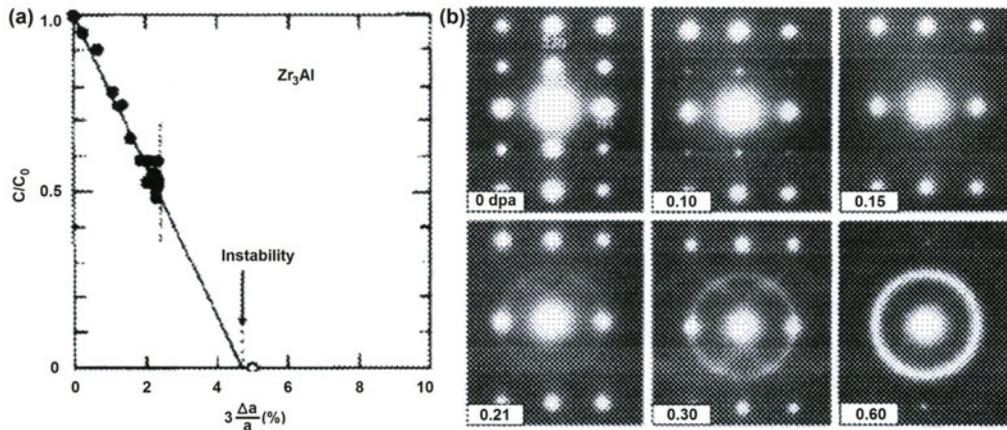
### 4.2 Experimental observations

#### 4.2.1 Indirect

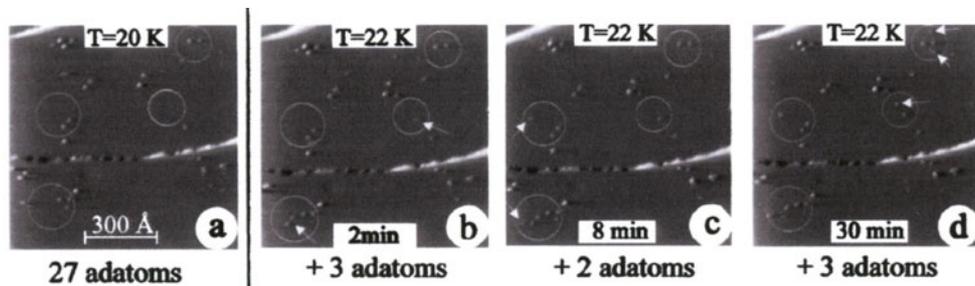
The large shear susceptibility was found with many related results summarized in a book by Robrock [21,22].

One of the most characteristic features of supercooled liquids and glasses is the temperature dependence of the viscosity, which can range over 28 orders of magnitude for a relatively small temperature range. A most fruitful concept, the fragility  $F = \partial\eta/\partial T$ , was introduced by Angell [23,24], and has been used in hundreds of articles since. It can be regarded as an extension of an earlier notion by Nemilov [25] to describe non Arrhenius behavior in oxide glasses. Angell pointed out the correlation of fragility with the discontinuity in the specific heat at  $T_g$ . A theory for this including the temperature dependence of the specific heat and the shear modulus change was given by Granato [26,27]. It is notable that  $\eta$  depends on  $G$ , and  $c$ , equation (6) whether the system is in equilibrium or not. The concept of fragility has had an enormous impact on the literature of glasses and amorphous materials, with two international conferences in the coming year alone dedicated to celebrate this and the many other seminal contributions of Angell.

Another much discussed feature arising from the resonance modes is the boson peak, found in the specific heat ( $C_p/T^3$ ) in most glassy materials near 10 K or below. There has been much confusion about this, in part arising from overlap with the simultaneous existence of a lattice dispersion peak a few degrees above the boson peak, found



**Fig. 7.** Irradiation of  $Zr_3Al$  [21]. (a) Shear modulus vs. lattice parameter change with irradiation. (b) Laue X-ray diffraction patterns as a function of displacements per atom (dpa).



**Fig. 8.** Appearance of migrating self-interstitial atoms at the surface at 22 K: (a) Pt(111) after  $Ne^+$  (4.5 keV) ion bombardment at 20 K,  $F = 1 \times 10^{11}$  ions/cm<sup>2</sup> ( $=9$  impacts/ $950 \text{ \AA} \times 950 \text{ \AA}$ ); (b)–(d) same surface area as in (a), but obtained after keeping the surface at 22 K for 2, 8, and 30 min, respectively. Circles mark the areas where additional adatoms (migrating interstitials) appear, and arrows show their first appearance. The time at the annealing temperature and the number of additional adatoms between two shown images are indicated. ( $U = 0.3$  V,  $I = 1$  nA).

by Harms et al. [28]. These can be distinguished by annealing, with the lattice dispersion peak increasing with annealing, while the boson peak decreases [29]. For this work, they prepared a single crystal of the material, so that the shear modulus in the crystalline state was a measured reference point. Schwarz also produced, with Johnson [30], the first bulk metallic alloys in the form of rods with a few mm diameter, allowing for the measurement of bulk properties such as the specific heat.

The fact that the shear modulus and volume change (Fig. 7a), as well as the Laue X-ray diffraction patterns (Fig. 7b) found by Okamoto et al. [31] show that the same properties found at low doses in radiation damage remain at doses four orders of magnitude larger is again evidence for the ITCM. The glass transition is not sharp, as in a phase transition, but gradual with increasing defect density, from characteristic crystalline Laue spots to amorphous ring patterns. For a certain range, both the Laue crystalline and amorphous rings appear simultaneously. This shows that the amorphous “phase” is a crystal containing a sufficiently large concentration of defects. This has been a stumbling block for many to overcome.

With the exception of the work by Khonik, Averbach, Kogure, and associates, the research was not done with

the intent of testing, or sometimes even knowledge of, the ITCM, but it provided strong evidence for it.

#### 4.2.2 Direct

The direct visual observation (Fig. 8) of interstitial diffusion to the surface in platinum near 20 K in irradiated thin films by Morgenstern et al. [20] using a variable temperature scanning microscope (STM) technique provides the most compelling evidence for the theory. The diffusion parameters (activation energy and frequency factor) are in good agreement with those found from resistivity annealing measurements after much higher doses by Dilibert et al. [32,33]. When the Okamoto et al. and Dilibert et al. experiments are added to the Morgenstern et al. experiment, these together provide a final proof for the ITCM.

## 5 Conclusion

In conclusion, a simple model for condensed matter is given by intrinsic interstitials in the interstitialcy configuration (ITCM). Good agreement with experiment

has been found quantitatively with properties of simple materials and also for complex alloys.

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