Practical applications of the electron theory to improve physical and mechanical properties of engineering materials

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A brief account is given of the origin and development of the electron theory and its successful application to improving physical and mechanical properties of a range of materials, including hard metals, metal–ceramic bonding, intermetallics and steels. As the nature of the bonding in solids, i.e. metallic, semi-conductor or insulator, determines both their mechanical and electronic properties, it is suggested that a theory linking both properties is desirable. The development of such a theory could be the basis of a better understanding of the mechanical properties of solids and the production of new materials for various technological applications.

1. Development of the electron theory

The foundation stone for the application of the electron theory to alloy design was laid by the British metallurgist William Hume-Rothery in 1926, based on studies conducted on certain alloys of the group IB (noble) metals in the periodic table of elements, i.e. Cu, Ag and Au. Hume-Rothery proposed that for these alloys there existed a correspondence between their crystal structures and the average number of valence electrons per atom, i.e. e/a ratio. Previously alloy formation, selection and composition was regarded as a trial-and-error, hit-or-miss affair. It is also remarkable that Hume-Rothery made his observations at the time when quantum mechanics was being developed by Schröedinger and others, as modern electron theory can be said to be well founded on the principles of quantum mechanics. Another important advance was made by Hägg [1] in 1929 on the structure of hard metals which form a part of the industrially valuable cemented carbides such as WC–Co cutting tool tips. Hägg was the first to state that for hard metals based on the carbides, borides and nitrides of the early transition metals of the periodic table (Table I), the ratio of the radii of metalloid to metal atoms determines the crystal structures of the compounds. Hägg stated that for metalloid to metal atom radius ratio less than 0.59, the metal atoms would be arranged in a close-packed structure; when the critical radius ratio of 0.59 was exceeded, the crystal structures would be complicated. Experimental results led Hägg to the conclusion that for critical radius ratios less than 0.59, metal atoms were in contact with the non-metal atoms, suggesting that the compounds would have a partly metallic and partly covalent bonding.

The development of quantum mechanics implied that information such as the equilibrium energy and other physical variables of a system (where a system in this case could be a single atom, molecule or compound) can be obtained by solving a Schröedinger equation for the system. However, the Schröedinger equation can be solved easily only for the hydrogen atom. For systems containing more than one electron, the Schröedinger equation becomes difficult to solve due to an electronic interaction term: correlation. Hatree [2] in 1928 tried to solve the Schröedinger equation for systems with more than one electron by making certain simplifying assumptions about the electronic interaction. The energies obtained by his method were usually in excess of those obtained experimentally. In 1930 Fock [3] tried to improve on Hatree's formulation by introducing an additional term, the exchange term, to take care of the Pauli exclusion principle, resulting in the Hatree–Fock approach. However, the results of his calculations did not agree with experimental results for many electron systems. Wigner & Seitz [4] in 1933 were able to solve the Schröedinger equation for sodium, obtaining a cohesive strength with some small deviation from the actual values. Their method worked well because of the monovalent nature of sodium, but attempts to apply the same method to polyvalent metals met with very little success.

Linus Pauling's [5] publication of the momentous text "The nature of the chemical bond" around 1939 was a great leap forward. Pauling showed in his text that guided by the principles of quantum mechanics and good physical intuition, very many important facts concerning bonding in solids could be deduced without the necessity for mathematical complexities. One of Pauling's original contributions was the suggestion that some of the five d-orbital electrons take part in bond formation in transition metals. Another interesting result of quantum mechanics is that an object such as an electron can be viewed either as a

TABLE I Transition metals of Groups III–VIII with elements of Groups IB and IIB.

Period 4	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
	$4s^2$	$4s^2$	$4s^2$	$4s^1$	$4s^2$	$4s^2$	$4s^2$	$4s^2$	$4s^1$	$4s^2$
	$3d^1$	$3d^2$	$3d^3$	$3d^5$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^{10}$	$3d^{10}$
Period 5	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
	$5s^2$	$5s^2$	$5s^1$	$5s^1$	$5s^2$	$5s^1$	$5s^1$	$5s^0$	$5s^1$	$5s^2$
	$4d^1$	$4d^2$	$4d^4$	$4d^5$	$4d^5$	$4d^7$	$4d^8$	$4d^{10}$	$4d^{10}$	$4d^{10}$
Period 6	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg
	$6s^2$	$6s^2$	$6s^2$	$6s^2$	$6s^2$	$6s^2$	$6s^2$	$6s^1$	$6s^1$	$6s^2$
	$5d^1$	$5d^2$	$5d^3$	$5d^4$	$5d^5$	$5d^6$	$5d^7$	$5d^9$	$5d^{10}$	$5d^{10}$
	$4f^{14}$	$4f^{14}$	$4f^{14}$	$4f^{14}$	$4f^{14}$	$4f^{14}$	$4f^{14}$	$4f^{14}$	$4f^{14}$	$4f^{14}$

wave or a particle; experimental results support both views. It also turns out that the conditions of the valence electrons in a solid determine the nature of its bonding. The valence electrons in solids are subjected to strong Bragg reflections similar to X-rays, and the planes that give the strong reflection in a particular crystal structure would normally form a set of polyhedra termed Brillouin zones in a space defined by the quantum momenta of the electrons in three dimensions, i.e. K-space (Fig. 1). A graphical representation of the possible momenta of electrons in an element in this K-space in three dimensions gives a Fermi surface, which in the simplest cases could be spherical. The interaction between this Fermi surface and the Brillouin zones has been used to differentiate an insulator from a metal and to explain phase transformations in alloys and intermetallic compounds [6, 7]. Mott & Hubbard [8], in a theory based on electron repulsion effects in solids, have identified the conditions under which an insulator would transform into a metal, based on the ionization energy (i.e. the ability to lose an electron) and, conversely, the ability to accept an electron, the electron affinity. The Mott–Hubbard model is a step ahead of the Brillouin zone theory, because it recognizes that the interatomic spacing in atoms is an important factor in determining whether they would form an insulator or a metal. The Mott–Hubbard model also prescribes a criterion for insulator–metal transition by alloying.

Engel & Brewer [9] also made a significant observation that group IB elements (Cu, Ag, Au) do not possess a filled outermost d-orbital in the metallic state. This is confirmed by the cohesive energies of these metals, clearly indicating that they do not have a filled outermost d-orbital. The development in the mid 1960s by Hohenberg, Kohn and Sham [10, 11] of the local density functional theory made the solution of the Schröedinger equation a practical reality for polyvalent metals and compounds. Since the development of the local density functional theory, condensed matter theorists have been able to extract information about bonding and crystal structures of metals and compounds, using the currently available high-speed computational techniques.

Villars [12] attempted to correlate the important variables in the Hume–Rothery criteria, i.e. electronegativity difference, atomic size difference and the average number of electrons per atom with the crystal structure exhibited by alloys and compounds based on

a three-dimensional plot. Villar's maps could not accommodate certain crystal structures because the coordinates had a classical rather than a quantum origin; classical coordinates are not appropriate for describing the behaviour of atoms and molecules. This has been remedied by Pettifor [13] who conceived an ingenious two-dimensional way of arranging the structures of compounds, based on the coordinate termed the Mendeleev number, which follows the ordering of elements in the periodic table, and therefore has a defined link with the quantum nature of atoms in compounds. Pettifor's structure maps have enjoyed tremendous success in predicting the structures of many compounds. In an analogous way, the authors of this article [14] have deduced a property field map, based on the number of d-state electrons in the orbitals of transition metals. The d-state electron orbital arises directly from the quantum-mechanical nature of atoms, and the use of the valence electrons that occupy this orbital removes a deficiency which would have existed if classical coordinates had been used. The various properties of transition metal compounds and alloys are found to partition into different regions within the two-dimensional plot. We envisage that an extension of this property field map into three-dimensions would open up a variety of useful alloy combinations for intermetallic compounds.

2. Electron–dislocation interaction

The motion of dislocations in solids is directly related to the state of the valence electrons in the solid. For pure metals in which the valence electrons form a sort of free electron pool, i.e. delocalized electrons, the stresses required for the motion of dislocations are low compared to those of ionic or covalently bonded solids in which the electrons are confined to certain directions (i.e. localized electrons). The general belief is that the bond breaking and remaking necessary for dislocation motion are much easier under a free electron configuration.

In relatively strongly bonded materials, it is possible to release localized electrons from their bound state by methods that include the supply of thermal energy or electrical energy. Alloying can also lead to an insulator–metal transition by increasing the free electron concentration. Troitskii & Likhtman [15] in the Soviet Union in the 1960s were the first to observe that a wind of electrons in a metal, generated by the
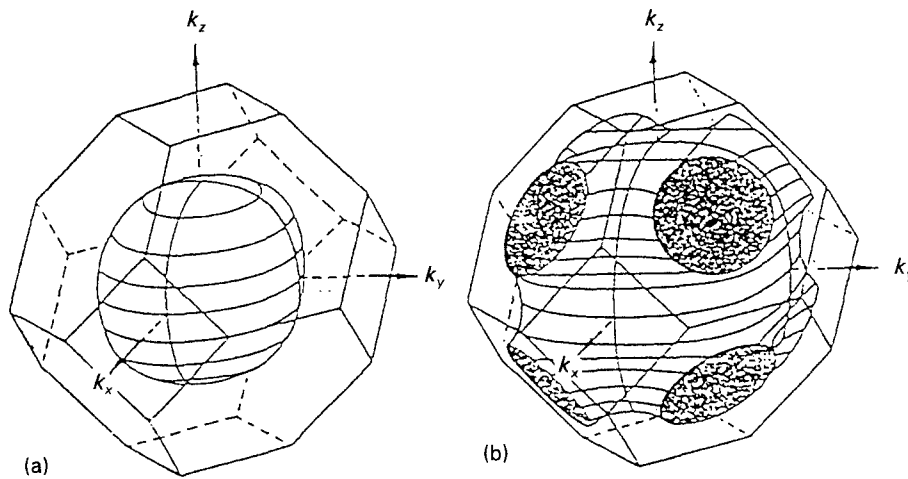
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Figure 1 The first Brillouin zone of a face-centred cubic structure with surfaces of constant energy of electrons shown for (a) nearly free electrons near bottom of zone and (b) electrons at zone boundary.

passage of an electric current, assisted dislocation motion; this effect was called an electroplastic effect. Troitskii and other Soviet workers [16] applied a high-density short-time d.c. pulse during metal working and observed a reduction in the force required for drawing metals; Hans Conrad and colleagues [17] in the USA have also observed this electroplastic effect in metals in the 1970s.

In the context of the link between dislocation motion and the electronic state, Gilman [18] has associated dislocation motion in silicon with the excitation of bonding electrons into antibonding states. He has also indicated that there is a correlation between dislocation glide activation energies and the average band-gap energy in solids. Recent experiments of Pharr *et al.* [19], in which silicon was observed to undergo an insulator–metal transition under an indenter load, was interpreted by Gilman as being due to the narrowing of the band-gap energy in silicon, thereby increasing the probability of electrons tunnelling from the valence band (bonding states) into the conduction band (antibonding states), resulting in metallization. A group of Chinese workers [20] have recently related bonding and ductility in the intermetallic compound TiAl by measuring the Debye temperature θ_D using X-ray diffraction methods; the high value of the Debye temperature θ_D of TiAl relative to pure Ti or Al was associated with the valence electron structure of TiAl. Their interpretation was based on the premise that the high ratio of covalent (bound) electrons to lattice (delocalized) electrons was responsible for the strong bonding and high value of θ_D in TiAl, compared to pure Ti or Al. It was their suggestion that a high θ_D affects the Peierls stress which is known to be sensitive to thermal energy fluctuations in a solid.

3. Applications of electron theory

3.1. Phase stability in alloys and compounds

Many recent attempts have been made to apply the electron theory approach to achieve a better understanding of phase transformation in alloys and compounds. One such area of application is in the martensitic transformation in shape memory alloys.

Recently, researchers [21] have studied the influence of the electron concentration in the Cu–Al–Mn alloy systems on the ultimate martensitic structure of the alloys. In the Cu–Al–Mn alloys studied, which had manganese contents in the range 4.4–61.7%, a relationship between the martensite phase structure and the electron concentration in the alloy was observed. The martensite structure was found to depend on the electron concentration (e/a); a value of e/a greater than 1.45 yielded the 2H structure, while for values less than 1.45 an 18R structure is stable. Other researchers [22] have proposed a model to explain the effect of manganese addition on the martensitic transformation temperatures in NiTi shape memory alloys. They argued that changes in the number of valence electrons were not the only important factors contributing to the value of M_s temperature, but also that changes in the d-band states played a significant role. Their model indicates the possibility of controlling the M_s temperature of NiTi when alloyed with manganese to a maximum of 2.5 wt %. In a similar vein, Japanese workers [23] have proposed a model for estimating the solubility limit and phase stability in transition metal-based alloys. They have suggested that a parameter, which represents the average energy level of the d-orbitals of the alloying transition metals, can be used to predict phase stability in transition metal-based alloys. This method was used to establish that the γ single-phase region in the Fe–Cr–Mn ternary system was not as broad as previously reported in the literature [24]; this approach was also applied to alloy design in Ni-, Co- and Fe-based superalloys [24]. Ahmed & Ahmed [6] have also recently separated the chemical free energy change associated with phase transformations in thallium and its dilute alloys into volume-dependent and volume-independent components. The volume-independent component was linked to the different energy levels occupied in the Brillouin zone of the crystal structures before and after the phase transformation.

3.2. Hard metals

The most successful hard metal cutting tool consists of a microstructure of tungsten carbide grains (hard

phase) embedded in a cobalt matrix (binder). The general instability in the global supply of cobalt has led many research efforts to utilize other carbides, such as TiC, TaC, etc., that may not require a cobalt binder. For many of the other carbides and borides of early transition metals that have been explored as replacements for WC, it has been difficult to find a suitable binder. The present authors [25–27] have proposed a model based on the unfilled d-orbital states of transition metals that provide rules in the binder selection procedure, when used along with thermodynamic and phase equilibrium data. The rules are based on a combination of contributions; a tight binding approximation model of bonding in transition metals due to Friedel [28], and an extension of a similar analysis to carbides, borides and nitrides of transition metals by Dempsey [29].

3.3. Metal–ceramic bonding

Li [30] has recently proposed a model aimed at elucidating the mechanism of bonding of metal to ceramic oxides. Li's model is based on the hypothesis that two major factors control the bonding of a metal to a ceramic oxide; firstly, that there must be a possibility of transferring electrons from the metal to the valence band of the ceramic, and secondly, the availability of holes in the valence band which can be considerably enhanced by increasing the temperature. The best metals for bonding to ceramic oxides would also generally have a high electron density. It has been generally observed by Li that when the above conditions are met, the work of adhesion between a metal and ceramic oxide increases considerably, with a corresponding lowering of the contact (or dihedral) angle at the metal–ceramic interface. Experimental confirmation of some of the above proposals can be found in the work of French [31] on bonding of Cu to Al_2O_3 films, based on experimental techniques like vacuum ultra-violet spectroscopy and valence band photo-emission spectroscopy.

3.4. Intermetallics

Transition metal aluminide intermetallics have recently achieved prominence because of their high promise for aerospace applications. There are many recent reviews on their properties, e.g. by Paxton [32] Yamaguchi & Umakoshi [33], Varin & Winnica [34], Cahn [35] and Froes et al. [36]. It is clear that one of the major problems confronting the applications of a special class of intermetallics (in the aerospace industry especially), is their intrinsic brittleness. An attempt to make these brittle intermetallics ductile, i.e. to 'metallize' them, is one area where the electron theory of metals has substantial promise. Pettifor's [13] structure maps based on the Mendeleev number could prove to be an essential starting point in this regard. In his structure maps, Pettifor has shown that there exists a possibility of moving from one structural domain (in binary intermetallic compounds) to another by the suitable addition of a third or more alloying elements. Pettifor cites the case of Al_3Ti

which changes from a tetragonal structure to the cubic Cu_3Au-type structure on alloying with the 3d elements Fe, Ni, Cu or Zn. While it is generally true that crystal structures with a higher symmetry, such as the cubic, are very likely to satisfy the von Mises criteria for arbitrary plastic strain and ductility, the brittleness of cubic $ScAl_3$ is a sure indication of the fact that the state of the valence electrons (i.e. whether localized or de-localized) would seem to be an equally, if not more, important factor in determining the ductility in intermetallics. Based on a slightly different analytical approach, Fu [37] has investigated the effect of electronic state on the brittleness of trialuminide alloys using the full-potential linearized augmented plane-wave (FLAPW) total energy method. Fu suggested that the brittleness of transition metal trialuminide alloys was due to the presence of strong directional bonds, high stacking fault energies and low cleavage strength. Fu further suggested that alloy additions to enhance dislocation dissociation could assist in improving ductility in these alloys. This has a great deal in common with the premise of Cottrell [38] who has shown how the electrostatic and band structure contributions affect the C_{44} crystal elastic constant and how this provides ductility in aluminium and brittleness in Al_3Sc and Al_3Ti. The properties which relate ductility or brittleness in solids are μ (the shear modulus) on the slip plane and K, the bulk modulus, both of which can be defined in terms of crystal elastic constants as

$$\mu = \frac{3C_{44}[C_{11}-C_{12}]}{4C_{44} + C_{11}-C_{12}} \qquad (1)$$

and

$$K = 1/3(C_{11} + 2C_{12}) \qquad (2)$$

where C_{ij} are crystal elastic constants. The ratio of μ/K is a good indicator of ductility or brittleness in cubic metallic crystals; a value of $\mu < 0.4$ corresponds to ductility and $\mu > 0.5$ corresponds to brittleness. It also transpires that the value of anti-phase boundary energy γ_{APB} can be estimated within the rigid sphere model [39] in terms of the crystal elastic constants. The present authors have proposed a model and a set of rules for improving the ductility of brittle intermetallics based on an interpretation of the electron theory [26, 40]. The rules which are based on the unfilled d-orbital electrons of the transition metal-based intermetallics used transition metal aluminide intermetallics as prototypes. One important result of the model was the observation of a correlation between the anti-phase boundary energy γ_{APB} of the transition metal-based intermetallics and d^+, the sum of the number of unfilled d-orbital state electrons in each constituent transition metal element in an intermetallic compound, of the form

$$\gamma_{APB} \propto \frac{1}{d^+} \qquad (3)$$

The proposed relationship is useful in the sense that it gives an indication of how the selection of alloying transition metals based on their unfilled d-state electrons can help to influence the anti-phase boundary

energy, which also affects superdislocation motion and the ease with which cross-slip can occur (i.e. induce ductility) in ordered intermetallic compounds.

3.5. Steels

Cottrell [41] has recently called for the development of an electron theory of steels to improve the understanding of quantum mechanical interactions due to the presence of solutes and other alloying elements in steels. A recent development by Chinese researchers [42] on the application of a semi-empirical electron theory model to explain the effect of alloying elements on phase transformation in steels would seem to be in line with Cottrell's call. Yu, quoted in [42], has proposed an empirical electron theory of solids and molecules which forms the basis for the application of the electron theory to describe phase stability and its dependence on alloying elements in steels, as developed by the Chinese school. Liu et al. [42] have applied Yu's hypothesis to explain the effect of the valence electron structure on the isothermal transformation kinetics in a steel described as 40CrNiMo austenite steel. In this model, it is proposed that if the alloying elements have a stronger affinity for carbon in the steels than they have for themselves, a strong covalent interaction between the alloying elements and the carbon atoms in the steels would lead to a short-range ordered clustering of the carbides of the alloying elements within the matrix of the steel. A strong covalent interaction would exist within this cluster, which would restrict the movement of its surrounding atoms, thereby constituting an obstruction to diffusion and phase transformation. This was used to explain the shift in C-curves in the 40CrNiMo steel during isothermal transformation. A similar analysis by Liu et al. was used to explain the presence of the characteristic 'nose' in C-curves in steels. The interpretation of Liu et al. seems a good attempt to explain the formation of TTT diagrams in terms of the valence electron structure of the alloys. There have been other attempts by researchers in the Chinese school [43, 44], to apply Yu's empirical electron theory of solids and molecules to a range of phenomena such as solute segregation in steels.

3.6. Ceramics

The present authors have also recently applied basic bonding theories to achieve clearer understanding of certain properties of ceramic materials [45, 46]. In the first effort [45], the Hubbard model [47, 48] is used to explain the effectiveness of transition/rare earth metal oxide sintering additives on the densification behaviour of Si_3N_4. It is envisaged that the model developed could be applied to select densifying additives for other ceramics. A second effort [46] examined the influence of electronic state on the resistance to the propagation of cavities in superplastic ceramics. It was deduced that ceramic materials which exhibit extensive superplastic deformation can do so by dislocation activation processes related either to an intrinsic 'metallic' character of their bonds, that can be ex-

plained within the Hubbard model [47, 48], or an extrinsic metallic character due to alloying, in which electrons can tunnel into the conduction band and activate dislocation motion. These dislocations provide the resistance to extension of cavities. Ceramic materials that lack either of the above 'metallic' characteristics in their bonds are less likely to be able to accommodate cavities during deformation, therefore remaining brittle.

3.7. Electron-continuum approach

Much of classical continuum mechanics is based on the adiabatic hypothesis of the Born–Oppenheimer approximation. This hypothesis is based on the assumption that the electrons are responsible for bonding between nuclei, but do not influence the dynamics of the nuclei within the lattice [49]. However, the adiabatic hypothesis of the Born–Oppenheimer approximation breaks down when there is a redistribution of electron states. A typical example would be the electron tunnelling in silicon, from the bonding to the anti-bonding states which Gilman [18] associates with dislocation motion and plasticity; another example would be the splitting of the Brillouin zone in ordered intermetallic compounds, which also influences the anti-phase boundary energy and therefore ductility. The adiabatic hypothesis imposes a very big limitation on the continuum theory of plasticity and makes the explanation of such phenomena as the electroplastic effect [15], the metallization of silicon [19] and other electronic state-dependent plasticity difficult to explain within the continuum theory of plasticity. There is a need for a new 'electron-continuum theory' that takes the effect of electron states, and their distribution, on lattice dynamics into consideration. Such a theory would represent a merger of the electron and continuum theories of solids.

Such a relationship can be conceptualized by an intuitive approach. In the same way that Einstein had to resort to the branch of mathematics called tensor calculus to find a suitable description in which space and time had a curved geometry (i.e. general relativity), theoretical mechanicists Kondo [50] and Bilby et al. [51] referred to this same branch of mathematics to describe a continuous distribution of dislocations in a solid using non-Euclidean geometry. Whereas one of the axioms of Euclidean geometry is that the sum of the interior angles of a triangle would be two right angles, in other systems of geometry describable by tensor analysis such as those of Riemann [i.e. Riemannian geometry] the above axiom of Euclidean geometry is found to be invalid. Kondo [50] and Bilby et al. [51], using tensor analysis, described a dislocation as a kind of torsion tensor which they defined as Cartan's torsion.

Another important concept from physics which has turned out to be a useful tool in theoretical continuum mechanics is that of the symmetrical properties of certain physical equations; these are expressed by a mathematical formulation called gauge groups. The gauge groups constitute an important method used by physicists to establish interactions between different

force fields. In the context of the gauge theory, the combination of a translational and rotational mode constitutes a gauge group in an elastic solid, as the equations of elasticity remain invariant under both transformations. Kadic & Edelen [52] have developed a gauge theory of dislocations by applying a mathematical operation, i.e. a gauge group, to an energy-related term called the Lagrangian that leaves the equations of continuum mechanics invariant under this mathematical operation. Golebiewska–Lasota [53] has developed this further to show that a close analogy exists in terms of an underlying mathematical symmetry between gauge transformations in electrodynamics and those of the continuum theory of dislocations in solids, based on the concepts described above. It is now intuitively possible to suggest a latent connection between the electronic state and the mechanical properties of solids, as the nature of the bonding (i.e. covalent, ionic or metallic) plays a key role in both the electronic-based and mechanical properties of solids. In this concept, the bonding in solids is considered as a sort of electromagnetic phenomenon. If the underlying link between electron states and their distribution and the mechanical properties in solids is fully realised, then it would be a unification which would have a tremendous effect on alloy design for various technological applications. A new quantum–continuum mechanics could then replace the current classical continuum mechanics.

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