

## Chemical Bonding in Aluminium and Its Influence on Precipitates in Al Alloys

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Understanding the nature and evolution of strengthening precipitates in aluminium alloys constitutes a major international research effort. The present work encourages a new perspective on precipitates in alloys by considering their morphology in relationship to the bonding electron density in the matrix. It considers a new experimental determination of bonding electron distribution in pure aluminium, in the context of its possible influence on precipitation. Correlations between the nature of a number of key strengthening precipitates and the bonding electron distribution have surfaced during this work that have never been considered, mainly due to of a lack of consensus on chemical bonding in aluminium over the last 70+ years. Accurate knowledge of chemical bonding in the matrix is also discussed in terms of developing analytical tools for solving the structure of precipitates with an atomic structure that is unresolved.

**Keywords:** *Chemical Bonds, Strengthening Precipitates, Electron Density, Quantitative Convergent Beam Electron Diffraction, Ab Initio Atomistic Modelling.*

### 1. Introduction

The crystallography and nano-structural evolution of strengthening precipitates in aluminium alloys is a subject that has attracted a considerable research focus. In many cases, the atomic structures of such phases are still not well understood. In efforts to develop refined methods of extending property profiles of aluminium alloys, atomistic modeling of the evolution of strengthening precipitates is playing an increasingly important role, alongside established empirical approaches, in directing alloy processing techniques. An accurate knowledge of precipitate structure and morphology is imperative in both cases. In addition atomistic modeling depends intimately on parameters that can only be obtained from knowledge of inter-atomic chemical bonding. Such parameters are almost always derived from solid-state theories such as density functional theory (DFT) or other self-consistent field (SCF) calculations.

All *ab initio* approaches have at their bases, the ground state electron density and the computation of this is heavily dependent on the basis functionals used for the calculations as well as the formalism chosen to account for exchange correlation in the case of DFT. Large discrepancies are reported throughout the scientific literature between varied applications of DFT and SCF calculations and this makes reliable atomistic modeling very difficult to achieve.

The bonding electron density in aluminium has been probed many times experimentally [1-10] and has also been derived frequently from *ab initio* theoretical models [10-14]. The main review on this subject [10] pointed out the significant discrepancies that exist between experimental measurements of electron density and the predictions made by theory. However, most results have suggested that the main concentration of bonding electron density occurs in the octahedral interstices of the fcc structure.

The present work originally set out to resolve the discrepancies in the literature by measuring the bonding electron density in aluminium with quantitative convergent beam electron diffraction (QCBED). This is now the most reliable technique for measuring Fourier coefficients of crystal potential (directly related to electron density) in solids with small unit cells [15]. These new measurements suggest that the bonding electron density is not concentrated in the octahedral interstices but in the tetrahedral interstices in fcc aluminium. This has led to the observation of a

number of correlations between the matrix bonding electron density and the nature of precipitates in aluminium alloys.

A new perspective on the relationship between precipitates and the host matrix based on chemical bonding is promoted in this work. The motive for this is the fundamental notion that all phase transformations require the breakage and reformation or at least the modification of chemical bonds between neighbouring atoms. That means that the formation of precipitate phases must at least in part be governed by the strength and anisotropy of chemical bonds in the host matrix.

## 2. Experimental Methods

A 99.9999+% pure aluminium foil was punched into 3mm diameter discs which were subsequently ground to  $150\pm 30\mu\text{m}$  in thickness and electropolished with a 33vol.%  $\text{HNO}_3$  - 67% methanol solution in a Struers Tenupol 5 twin jet electropolisher at a temperature of  $-20\pm 3^\circ$  and a potential difference of 12V. A total of 60 CBED patterns from five different zone axes, different scattering geometries and different specimen thicknesses were acquired at 120kV and 200kV with a JEOL 2011 transmission electron microscope (TEM). From these, a total of 1095 pattern-matching refinements were carried out using the QCBED method [16] to refine the 14 non-equivalent structure factors.

## 3 Results: Electron Distribution in Pure Aluminium

Bonding electron densities are determined by calculating the difference between experimentally measured total electron densities and those derived from the independent atom model (IAM – does not account for chemical bonding). The EDEN Crystallography package by Somoza et al [17] was used to perform holographic reconstruction of the total electron density [18] using the structure factors measured in the present work and those of Raccah and Henrich [5]. The latter were referenced by review articles as the most accurate measurements of structure factors in aluminium at the time [10]. The electron density derived from the IAM using Doyle and Turner scattering factors [19] was also calculated in the same manner and subtracted from each of the experimental determinations in turn to produce the deformation electron densities,  $\Delta\rho$ , displayed in Fig. 1.

The immediate distinction between the separate determinations of bonding electron density,  $\Delta\rho$ , is the concentration of bonding electrons in the tetrahedral interstices of the fcc structure of aluminium as determined by the present work. The work of Raccah and Henrich [5] was chosen for comparison because it typifies many results in the literature that suggest that bonding electrons concentrate dominantly in the octahedral interstices. All of the published theoretical results [10 – 13] agree more closely with this latter view of the bonding electron distribution, when published structure factors have been used to compute the bonding electron density in the same manner as above.

This places the present results at odds with more than half of the experimental measurements made by X-rays and all of the theoretical determinations. Of the three experimental determinations by X-rays that were found to agree with the present work, only one involved the measurement of more than the three lowest-order structure factors [9]. The lack of range in the other two sets of measurements [3, 4] does not, however, invalidate such results as the primary bonding density information is always held in the lowest order structure factors. In fact, truncation of the data sets of the present work and that of Raccah and Henrich [5], used for Fig. 1, to the three lowest-order structure factors yields, morphologically, the same distribution of bonding electrons as presented in Fig. 1. The general trend in the literature, however, is one that supports a higher bonding charge density in the octahedral interstices as per the right-hand side of Fig. 1. A recent example of this is a study of the ideal shear strength of aluminium and copper as determined by various *ab initio* models that suggested that the chemical bonding in aluminium is octahedrally-coordinated [14].

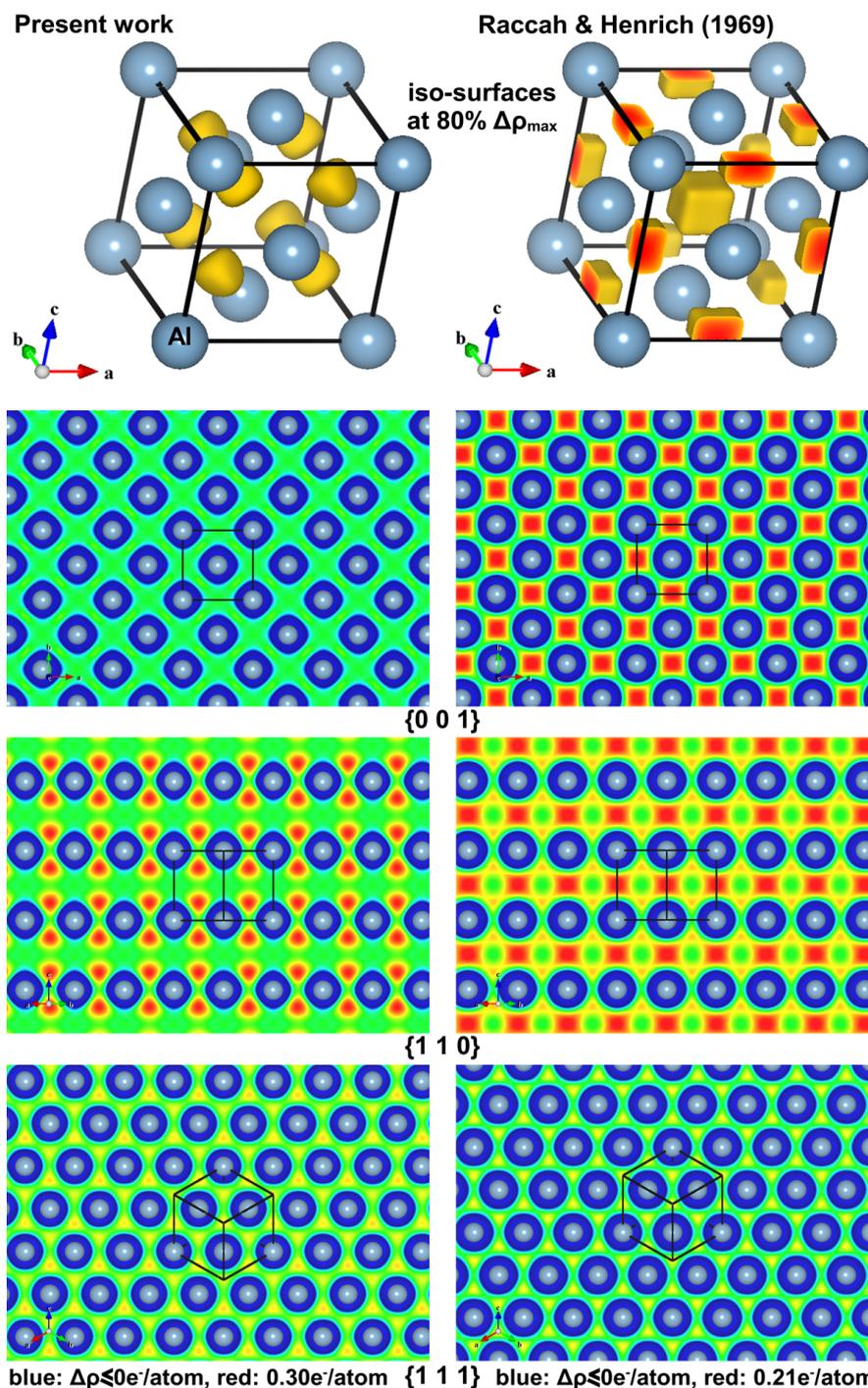


Fig. 1: The bonding electron density measured in the present work constitutes the left-hand half of the figure and is compared to the results of X-ray diffraction by Raccah and Henrich [5] in the right half. The plane sections (as indexed) and 3-dimensional models of the cell for each case were plotted with the VESTA visualization software by Momma and Izumi [20]. Unit cell outlines are shown in each component of the figure. The electron densities were computed using the holographic reconstruction method of Szoke [18], using the EDEN package of Somoza et al [17].

Returning to Fig. 1, the direct result of tetrahedrally-coordinated bonding is a low bonding electron density in  $\{0 0 1\}$  planes with moderate bonding in the  $\{1 1 1\}$  planes and the highest bonding density in  $\{1 1 0\}$  planes. This is in contrast to octahedrally-coordinated bonding which would suggest equally strong bonding in both the  $\{0 0 1\}$  and  $\{1 1 0\}$  planes with the weakest bonding in  $\{1 1 1\}$  planes. These results can now be compared and rationalized with respect to the observed nature of precipitates that form with large planar facets parallel to low-index planes in the fcc Al matrix.

## 4 Discussion

### 4.1 Correlations Between Bonding in the Matrix and Precipitates

Classically, the equilibrium form of an embedded precipitate particle is regarded [21] as being the product of a competition between the interphase (interfacial) energy and a shape-dependent strain energy. The thin plate-shaped form, that is common to precipitates in a range of high-strength aluminium alloys, is expected when the specific interfacial energy is small and the need to accommodate elastic strain energy, associated with changes in shape and volume, is dominant. The preferred coherent planar facet (or habit plane), for a given precipitate structure, will be that which defines an absolute minimum in strain energy. With this as framework, it is interesting to note that reasonably strong correlations between the matrix bonding electron density and morphologies of strengthening precipitates supported by the matrix become apparent in the present work. From the point of view of pure bonding electron distribution, planes that have the lowest bonding electron density might be deemed most conducive to the accommodation of precipitates given that less energy is required to rearrange bonding electrons in such planes.

If one adopts octahedrally-coordinated chemical bonding as per most of the literature, including the results of Raccach and Henrich [5] in Fig. 1, then it would appear that precipitates that have their main facets coplanar to  $\{0\ 0\ 1\}_{\text{Al}}$  and  $\{1\ 1\ 0\}_{\text{Al}}$ , would be the most difficult to form and that these planes also constitute directions in which growth of precipitates is most difficult. This contradicts what is generally observed in the literature for precipitates with main facets coplanar to  $\{0\ 0\ 1\}_{\text{Al}}$  [22–25], which happen to be quite common. The wide acceptance of octahedral bonding has therefore never led to the view that bonding electron density and precipitate morphology and formation have any significant correlation.

On the other hand, if one considers the bonding in aluminium to be tetrahedral, correlations become quite obvious. For example, GP zones form with great ease on  $\{0\ 0\ 1\}_{\text{Al}}$  planes and are very difficult to stop from forming in copper-containing aluminium alloys. This can be explained by the very low bonding electron density that exists in  $\{0\ 0\ 1\}_{\text{Al}}$  planes as seen in the left-hand side of Fig. 1. GP zones have very high aspect ratios as substitution of Al atoms by Cu atoms within a single  $\{0\ 0\ 1\}_{\text{Al}}$  plane would not require as significant a rearrangement of electron density as adding additional layers of Cu atoms. This is because growth perpendicular to  $\{0\ 0\ 1\}_{\text{Al}}$  would involve perturbation of strong bonding electron density in two sets of  $\{1\ 1\ 0\}_{\text{Al}}$  planes that lie perpendicular to  $\{0\ 0\ 1\}_{\text{Al}}$ . Another precipitate phase forming its main facet coplanar to  $\{0\ 0\ 1\}_{\text{Al}}$  is  $\theta'$  [22–25]. This phase does not form as easily as GP zones because the latter are formed substitutionally (i.e. there is no change in the underlying crystal structure) whilst  $\theta'$  involves the formation of an altogether new crystal lattice. This implies a much more significant rearrangement of bonding electron density. The coherence of this structure with  $\{0\ 0\ 1\}_{\text{Al}}$  means that the main facet of  $\theta'$  precipitates is coplanar to  $\{0\ 0\ 1\}_{\text{Al}}$ , but again, the resistance posed by the strong bonds in two sets of perpendicular  $\{1\ 1\ 0\}_{\text{Al}}$  planes could be seen to contribute to the formation of high aspect ratio precipitates.

The precipitates with the highest aspect ratios in aluminium alloys correspond to the  $T_1$  and  $\Omega$  phases that form in Al-Cu-Li and Al-Cu-Mg-Ag alloys [22–24]. Precipitates of these phases form with main facets along  $\{1\ 1\ 1\}_{\text{Al}}$  planes. From the bonding electron density determined in the present work, one could guess that these precipitates are more difficult to form than GP zones and  $\theta'$ , not only due to the formation of a lattice that differs from the matrix but also because of the higher bonding electron density that exists in  $\{1\ 1\ 1\}_{\text{Al}}$  planes as compared to  $\{0\ 0\ 1\}_{\text{Al}}$ . The high aspect ratios of  $T_1$  and  $\Omega$  precipitates, however, is of particular interest to the aluminium alloys community [23, 24]. A rationale based on bonding electron density would be that there are 3  $\{1\ 1\ 0\}_{\text{Al}}$  planes perpendicular to any  $\{1\ 1\ 1\}_{\text{Al}}$  plane. To perturb the high bonding electron density in three such planes is much more difficult than to perturb the electron distribution within  $\{1\ 1\ 1\}_{\text{Al}}$

planes. This means that growth of these precipitates will be heavily favoured coplanar to  $\{1\ 1\ 1\}_{\text{Al}}$  but severely restricted in the perpendicular direction.

One might go even further and compare aspect ratios of various precipitate phases forming with main facets on different matrix planes, for example,  $T_1$  and  $\theta'$ . In the case of  $\theta'$ , there are only two  $\{1\ 1\ 0\}_{\text{Al}}$  type planes that are perpendicular to a  $\{0\ 0\ 1\}_{\text{Al}}$  type plane with which the main facet of  $\theta'$  is coplanar. Thus, thickening of  $\theta'$  could be expected to be easier than thickening of  $T_1$  where there are three  $\{1\ 1\ 0\}_{\text{Al}}$  type planes perpendicular to a  $\{1\ 1\ 1\}_{\text{Al}}$  type plane with which the main facet of  $T_1$  is coplanar. It is apparent [22–25] that  $\theta'$  does in fact form precipitates with smaller aspect ratios than  $T_1$ .

As far as the authors are aware, there are almost no precipitate phases with main facets coplanar to  $\{1\ 1\ 0\}_{\text{Al}}$ . The closest such habit, orientationally, occurs for the S phase with a main facet coplanar to  $\{2\ 1\ 0\}_{\text{Al}}$  [24, 26]. Had Fig. 1 been extended to show the bonding electron density in this plane, the observed correlation between tetrahedrally-coordinated bonding electron density and precipitate morphology would be seen to remain intact as the bonding electron density in  $\{2\ 1\ 0\}_{\text{Al}}$  is comparable to that in  $\{1\ 1\ 1\}_{\text{Al}}$  and is much lower than that in  $\{1\ 1\ 0\}_{\text{Al}}$ . This, however, is not the case if the view of octahedrally-coordinated bonding is taken.

#### 4.2 Determining the Structure of Precipitate Phases

The question of how to probe the structure of precipitate phases *in situ* is a salient one as one has no way of knowing whether their structures would remain unchanged in the absence of the supporting matrix. Given these entities are far smaller than any X-ray probe and that electrons interact between 3 and 4 orders of magnitude more strongly with matter than other forms of radiation, convergent beam electron diffraction becomes the most obvious choice. The ability to focus electron probes to sub-Ångstrom dimensions also provides the unique ability to single out individual precipitates and even individual columns of atoms for probing. The most likely approach to unequivocally solving precipitate structures, like that of the  $T_1$  phase, is described schematically in Fig. 2.

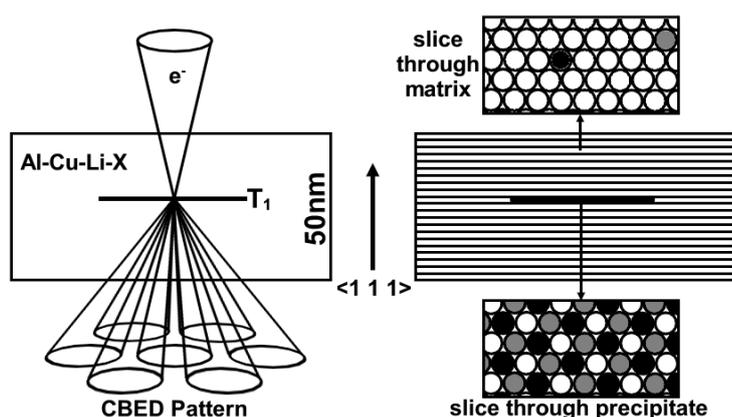


Fig. 2: A  $T_1$  precipitate surrounded by the matrix solid solution is probed by CBED. The CBED pattern will be dominated by scattering from the matrix with small perturbations from the precipitate. The multislice theory [27] involves dividing the probed material into slices of atomic thickness. Most of the slices constitute the matrix whilst only a few correspond to the precipitate. The atomic arrangement in the precipitate slices can be manipulated to refine the fit between a multislice-calculated CBED pattern and the experimental one, until the perturbations due to the precipitate have been matched, yielding the refined atomic structure associated with the precipitate.

At the heart of any such approach must be an accurate knowledge of the bonding electron density in the matrix. This is because the volume of the precipitate from which the electron beam scatters is hundreds of times smaller than the probed volume of precipitate. In order to be able to resolve and accurately pattern match the scattering due to the precipitate, the scattering from the matrix will need to be modeled with greater than 99% accuracy. Given that chemical bonding causes perturbations of the order of several percent, an accurate determination of the matrix bonding electron density is mandatory prior solving precipitate structures reliably.

## 5. Conclusions

A consideration of bonding electron density in pure aluminium, measured accurately with quantitative convergent beam electron diffraction [16], has led to the observation of significant correlations between chemical bonding within the aluminium host matrix and the nature of precipitates in aluminium alloys. The present electron density measurements stand in contrast to the majority of previous determinations by both experiment and theory, which generally support the view of octahedrally coordinated chemical bonding. The present view of tetrahedrally coordinated bonding in aluminium has been applied to explaining the morphological nature and growth of a small set of example precipitates in aluminium alloys. Furthermore, it is imperative that an accurate knowledge of the matrix electron density be acquired prior to a reliable determination of atomic structure in precipitate phases, particularly those with very high aspect ratios like T<sub>1</sub>.

Future work motivated by the present results includes the comparison of numerous calculations of the bonding electron density in aluminium derived from DFT and other SCF formalisms, with the present experimental determinations. It will be important for future atomistic modeling of precipitate evolution to be fed with accurate parameters obtained from experimentally benchmarked *ab initio* calculations of the bonding electron density.

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