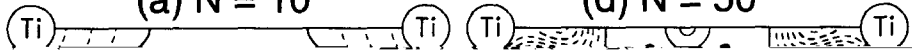


Fourier Synthesizing $\Delta\rho_{\text{calc}}(r, G_{\text{max}})$

(a) $N = 10$

(d) $N = 50$





lattice constants are roughly 9.4% larger than that of NiAl. This reflects the fact that Ni has a nearly full (more localized) d shell (atomic configuration [Ar]3 d^8 4 s^2), so its nuclear charge is better screened by the d shell relative to Ti. Figure 5(d)–(f) gives contour plots of the DEDD, while Fig. 8(c) gives the total density. Considering first the *total* density, we see similar features in TiAl [Fig. 8(a)] and NiAl [Fig. 8(c)]. Also, considering the DEDD maps (Fig. 5) we see that in the mixed transition metal–Al plane [parts (a) and (d) of Fig. 5] and in the Al plane [parts (b) and (e) of Fig. 5] the DEDD of NiAl and TiAl are practically similar. However, the transition metal plane [parts (c) and (f) of Fig. 5] show significant differences in the DEDD: In TiAl the t_{2g} -like (d_{xy}) lobes pointing *towards* the nearest Ti sites are *positive* and the e_g -like ($d_{x^2-y^2}$) lobes pointing in *between* the nearest Ti sites [towards the next nearest (NN) Ti along [100] and [010]] are *negative*. In NiAl the situation is reversed. This qualitative difference in the DEDD between the next nearest neighbor transition atoms can be seen more clearly in the line plot of Fig. 8(b) and (d): while in TiAl there is a *depletion* of charge in the region $0.2 \text{ \AA} < r < 1.0 \text{ \AA}$, in NiAl there is *charge accumulation* there. Furthermore, in the

maps are insensitive to the use of RHF or LDA reference atomic superposition charge densities.

(iii) While the *truncated* DEDD in the mixed Ti–Al plane captures roughly the main feature of the full DEDD, in the Ti-layer, truncated DEDD completely misses the directional features of the full DEDD. Many more structure factors than currently accessible will be needed to observe directional d bonding in measured DEDD maps.

(iv) The presently calculated valence charge density and DEDD are in good agreement with previous calculation of Fu *et al.* [23, 24]. However, our total charge density map differs substantially from that of Eberhart *et al.* [26]. Their arguments on the relationship between brittleness/ductility and the topological features of the charge density are not supported by our calculation.

(v) The main bonding features in TiAl can be described as (a) non-spherical charge depletion from both Al and Ti atomic sites (recall that in B2 NiAl, the Ni atom gains charge while Al loses charge [14]), (b) redistribution of charge such that there is considerable build-up of electrons between nearest-neighbor Ti atoms in all-Ti (001) planes, (c) a smaller charge build-up between second nearest-

interstitial region ($r \sim 2 \text{ \AA}$) there is charge *accumulation* in TiAl but *depletion* in NiAl. Note that while the total charge density [Fig. 8(a) and (c)] exhibit local minima in the midpoint between the transition metal atoms for TiAl and NiAl, the DEDD exhibits a local maximum for TiAl but a local minimum (with a small bump) for NiAl. This qualitative difference

neighbour Al atoms in all-Al (001) planes is simply metallic.

(vi) While TiAl exhibit strong nearest-neighbor bonding in the Ti plane, the hypothetical L1₀ form of NiAl has strong bonding in the *second* nearest-neighbor Ni plane. Indeed, TiAl shows a charge depletion near the atomic sites in the [100] direction

