Ductile Rare Earth Intermetallic Compounds

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For FY2003-2005 –

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ABSTRACT AND BACKGROUND

This effort is focused on gaining a more detailed fundamental understanding of the electronic, physical, mechanical and chemical factors leading to the unusually high room-temperature ductility found in certain stoichiometric rare earth intermetallic compounds. In particular, the aim is to understand the fundamental difference between RM compounds (where R = rare earth and M = a late transition or main group metal), where ductility is easily attained, and other intermetallic compounds, where ductility is seen only under special circumstances.

As part of this effort, first-principles electronic structure techniques are used to study the phase stability, elastic constants, and defects in these ductile B2 compounds. Interestingly, our calculations show that both the elastic properties and stacking fault defects on the {110} planes are significantly different from brittle counterparts, in particular NiAl. We have shown that the low defect energies on this plane are related to both the observed <001> slip on this plane, and the close competition between the B2 CsCl structure and the orthorhombic B27 and B33 structures.

TECHNICAL HIGHLIGHTS

- Calculated elastic constants, defect energetics, and phase stabilities within selected rare earth ductile B2 compounds, which provided insights to the unusual behavior in these systems.
- Theoretical analyses revealed that ordinary dislocations in the rare earth B2 compounds YCu, YZn and YAg are intrinsically different from the common B2 intermetallic alloys, such as NiAl.
- ASTM tests E 399-90 and E 813-89 were applied to three B2 rare earth intermetallic compounds: YCu, YAg and DyCu. Unusually high fracture toughness values were obtained for all three of the B2 compounds tested. The highest value measured (25.5 MPa$\sqrt{m}$ for DyCu) is similar to that of some commercial aircraft aluminum alloys.
- TEM examination of plastically deformed, single-crystal DyCu B2 intermetallic compound revealed bands of a second phase in the B2 matrix. Although the bands resembled twins, selected area electron diffraction showed that they possess an orthorhombic crystal structure with lattice parameters of a = 1.22 nm, b = 0.80 nm, and c = 0.38 nm.
- Certain rare earth B2 intermetallic compounds have been found to to be brittle. These include YMg and $(Tb_{0.88}Dy_{0.12})Zn$. It is hoped that further study of these "exceptions to the rule" will provide insights into the cause(s) of the high ductility seen in most rare earth B2 intermetallics.

INTERACTIONS WITH OTHER PROJECTS AND PROGRAMS

S. Agnew (Univ. Virginia) twinning; A. Bastawros (Iowa State Univ.) nanoindentation; E. George (ORNL) environmental embrittlement; Y. Grin (Max Planck Inst.) electron localization function

calculations; J. Kruzic (Oregon St. Univ.) fatigue; P. Nash (Ill. Inst. Tech.) thermodynamic studies to obtain heat and free energies of formation. Some of the work by J. R. Morris is supported through the "Alloy Behavior and Design" project supported by BES through Oak Ridge National Laboratory.

SELECTED PUBLICATIONS

K.A. Gschneidner, Jr., A.M. Russell, A.O. Pecharsky, Z. Zhang, T.A. Lograsso, J.R. Morris, D.K. Hsu, C.H.C. Lo, Y.Y. Ye, A.J. Slager, and D.C. Kesse, "A New Family of Ductile Intermetallic Compounds," *Nature Mater.,* **2**, 591 (2003).

A.M. Russell, Z. Zhang, T.A. Lograsso, C.H. Lo, A.O. Pecharsky, J.R. Morris, Y. Ye, K.A. Gschneidner, Jr., and A.J. Slager, "Mechanical Properties of Single Crystal YAg," *Acta Mater.*, **52**, 4033 (2004).

A.M. Russell, Z. Zhang, T.A. Lograsso, K.A. Gschneidner, Jr., A.O. Pecharsky, A.J. Slager, and D.C. Kesse, "Mechanical Properties of Single Crystal YCu and $(Tb_{0.88}Dy_{0.12})$Zn B2 Intermetallic Compounds," *Intermetallics*, **13**, 571 (2005).

A.M. Russell, "A Review: Ductility in Intermetallic Compounds," *Adv. Eng. Mater.*, **5**, 639, (2003).

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Y.R. Morris, Y.Y. Ye, Y.B. Lee, B.N. Harmon, K.A. Gschneidner, and A.M. Russell, "*Ab Initio* Calculation of Bulk and Defect Properties of Ductile Rare-Earth Intermetallic Compounds," *Acta Mater.*, **52** 4849 (2004).

Ductile Rare Earth Intermetallic Compounds

Personnel: K.A. Gschneidner, Jr. (co-lead PI), A.M. Russell (co-lead PI), D.J. Barnard (Asst. Scientist), A. Becker (Grad. Student), G. Cao (Postdoc.), C.H.C. Lo (Asst. Scientist), T.A. Lograsso (PI), B. Stumphy (Grad. Student), A.O. Tsokol (Asst. Scientist), and D. Wu (Asst. Scientist)

Scope:

Polycrystalline intermetallic compounds usually possess little or no tensile ductility at room temperature if they are fully ordered and exactly stoichiometric. However, high ductility has been observed in rare earth intermetallic compounds that possess the B2 (CsCl-type) crystal structure. This project seeks to determine the fundamental cause(s) of the anomalously high ductility in these rare earth compounds. Five hypotheses have been proposed to account for the high ductility, and these are being tested from a primarily experimental standpoint initially by transmission electron microscopy and mechanical properties measurements on single-crystal and polycrystalline specimens.

Research Highlights:

In 2000, Ames Laboratory scientist K. Gschneidner discovered that the intermetallic compound ErCu possesses unusually high ductility. ErCu is a "line compound" with the B2 (CsCl-type) crystal structure. A survey of 11 other binary B2-structure rare earth–non rare earth (RM) intermetallic compounds (YAg, YCu, DyCu, CeAg, ErAg, ErAu, ErIr, HoCu, NdAg, YIn, YRh) showed that all are ductile. Since 120 B2 RM compounds are known to exist, it is possible that many of these, possibly all, are similarly ductile.

Tens of thousands of binary intermetallic compounds are known, but studies by other investigators show that only a few dozen of them have appreciable room temperature ductility. That ductility is usually achieved by contrivances such as testing single crystals; testing in zero-humidity atmospheres; using a material that deviates from exact stoichiometry or a material with a metastable disordered structure; adding dopants such as B; or exploiting martensitic transformations that occur near room temperature to achieve ductility. None of these contrivances is necessary to confer ductility on the RM compounds; they are inherently ductile. However, the underlying mechanisms affecting this ductility are currently not understood.

The figure below compares the stress-strain curve of polycrystalline YAg to that of a common commercial Al alloy (3105). The 20% elongation of the YAg specimen is unusually large for an intermetallic compound; most polycrystalline intermetallics would elongate just 0 to 1% before fracture. The figure also shows a TEM micrograph of plastically deformed YAg, showing extensive dislocation structure in the deformed metal.

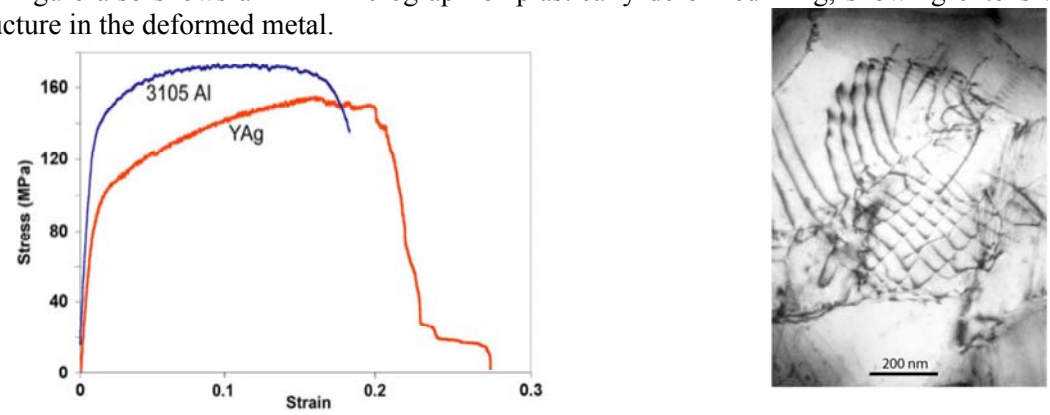


Fig. - (left) Comparison of the tensile test stress-strain plots of polycrystalline YAg intermetallic and commercial Al 3105 alloy; (right) TEM micrograph of dislocations in plastically deformed YAg.

We propose the following five hypotheses to possibly explain the high ductility of the rare earth intermetallics, and our research plan is designed to systematically test these hypotheses:

1. Grain boundary sliding - When recrystallized, RM intermetallics' fine grain sizes (200 to 500 nm) might allow deformation by grain boundary sliding. If so, the material would have high strain rate sensitivity; however, our tests on YAg show low strain rate sensitivity.
2. <111> slip - The <100> slip most common in B2 crystals fails to satisfy the von Mises criterion for extensive polycrystalline ductility. However, TEM $\mathbf{g}\cdot\mathbf{b} = 0$ analysis of YAg and YZn shows many dislocations with <111> Burgers vectors. This <111> slip presumably improves ductility.
3. Twinning- or transformation-assisted slip - Some metals are ductile even though their active slip systems do not satisfy the von Mises criterion. Their ductility arises from stress-induced twinning or phase transformations that re-orient available slip systems or accommodate strain incompatibilities near grain boundaries to facilitate extensive plasticity. Some RM intermetallics show serrated yielding, possibly from twinning or stress-induced phase transformations.
4. Dislocation energies intrinsically different from common B2 intermetallics - Theoretical calculations (see write-up by Biner and Chen in this section) show that cross slip should be much easier in RM compounds than in other common B2 materials (e.g., NiAl) because dislocation line tensions are nearly isotropic in the rare earth intermetallics.
5. Chemical factors associated with environmental embrittlement - The high rare earth content of these intermetallics may alter the environmental embrittlement reaction ($M + H_2O \rightarrow MO + 2H$) that degrades ductility in other intermetallics (e.g., FeAl) in humid air. The rare earth element may form hydrides that retard H diffusion along grain boundaries, thereby improving ductility.

Impact:

Intermetallic compounds typically possess strength, stiffness, corrosion resistance, and hot strength superior to ordinary metals. However, their room temperature brittleness and poor fracture toughness severely restrict their use. Better understanding of the anomalous ductility and high fracture toughness in RM compounds may lead to "ductilizing strategies" in other intermetallics that would permit wider application of these potentially useful materials.

Future Work:

Hypothesis #1 will be tested by further strain rate sensitivity testing of several RM compounds. Hypothesis #2 will be tested by further $\mathbf{g}\cdot\mathbf{b} = 0$ analysis of RM compounds and by continuing attempts to find single-crystal slip lines from <111> slip. Hypothesis #3 will be tested by tensile testing special strain stage TEM specimens while observing them in the TEM and by continued search for twins and second phase regions in deformed RM compounds. Hypothesis #4 will be further explored by continued calculation of dislocation behavior in RM compounds and observation of dislocation interactions by TEM. Hypothesis #5 will be examined by tensile testing RM compounds in the ORNL ultra-low humidity environmental tensile test facility and by searching for hydrides and a ductility loss in RM compounds strained in humid air.

Interactions:

S.B. Biner (Ames Laboratory) dislocation interactions; J. Morris (ORNL) and Y. Ye (Ames Laboratory) *ab initio* calculation of elastic constants and energies of formation; S. Agnew (Univ. Virginia) twinning; A. Bastawros (Iowa State Univ.) nanoindentation; E. George (ORNL) environmental embrittlement; Y. Grin (Max Planck Inst.) electron localization function calculations; J. Kruzic (Oregon St. Univ.) fatigue; P. Nash (Ill. Inst. Tech.) thermodynamic studies: heat and free energies of formation.

Stability of Ordinary Dislocations in Ductile Rare-Earth Intermetallic Compounds: YCu, YAg and YZn

Personnel: S.B. Biner (PI) and Q. Chen (Graduate Student)

Scope:

We evaluated the stability of ordinary dislocations, interaction energy of kink pairs, cross-slip behavior of screw dislocations, and the instability of pinned dislocations in ductile rare-earth intermetallic compounds: YCu, YAg and YZn. The results indicate that the elastic anisotropy does not cause any instability of ordinary dislocations in YCu, YAg and YZn as opposed to NiAl and Fe-25Al. The cross-slip characteristics and the external driving force required for the instability of pinned dislocations also differ considerably, resulting from their lower energy and the absence of negative line tension vis-a-vis for NiAl and Fe-25Al.

Research Highlights:

The recently discovered new class of intrinsically ductile intermetallic compounds which have the B2 crystal structure are based on the rare-earth element and late transition metal or an early p-element [1]. There are 120 such alloys; most of these have not been studied, but at least 12 have been found to be have significantly high ductility and fracture toughness in polycrystalline form when tested in room temperature and in air. Several investigators have examined the dislocation substructures in B2 intermetallic single crystals, such as NiAl. The emerging observations from these studies are: (1) The deformation at room temperature occurs exclusively by **b**=<001> dislocations gliding on {100} and {110} planes. When the orientation is along the hard [001] direction, the resolved shear stress for dislocations with **b**=<001> is always zero. However, slip on $<111>(1\bar{1}0)$ systems is also observed. (2) <001> dislocations near screw orientations exhibit 'zigzag' configurations and also a high density of jogs has been observed on zigzag dislocation segments.

The stability of dislocations in intermetallics plays an important role in deformation mechanisms for yielding and work hardening. The elastic energy, E, per unit length of a straight dislocation in a linearly anisotropic elastic crystal is given by:

$$E = \frac{K\, b^2}{4\pi} \ln\left(\frac{R}{r_0}\right)$$

where K is the energy factor for the dislocation, a function of both the elastic constants of the anisotropic crystal and the orientation of the dislocation line with its Burgers vector; R is the outer radius of integration; and r_0 is the dislocation core radius, which is of the order of the Burgers vector b. For isotropic elasticity, K simply scales with shear modulus, Poisson's ratio, and the angle θ between the dislocation line and the Burgers vector. For anisotropic elasticity, its determination requires numerical approaches, and can be evaluated by using either the sextic formalism or the integral formalism. In this study we adopted the sextic formalism given by Stroh [2]. The line tension per unit length of a straight dislocation depends on the energy factor K and its second derivative with respect to θ. If the logarithmic term is assumed to be constant for all dislocation orientations, the 1/K plots are equivalent to the inverse Wulff plots (1/E). There are two criteria for dislocation line instability: (1) the concavity of the inverse Wulff plot; and (2) the negative line tension, which is a sufficient but not a necessary condition for instability.

In the case of (001)[010] slip, as seen in Fig. 1, Fe-25Al exhibits instability in two angular ranges, one in a screw orientation (θ=0°) and the other in a mixed orientation ($\theta \approx 60°$), while for NiAl the instability range is only in the pure screw orientation. However, for this slip system and in others, we did not

observe either concavity in the (*1/K*) plot or negative values for the line tension in YCu, YAg and YZn, as can be inferred from Fig. 1.

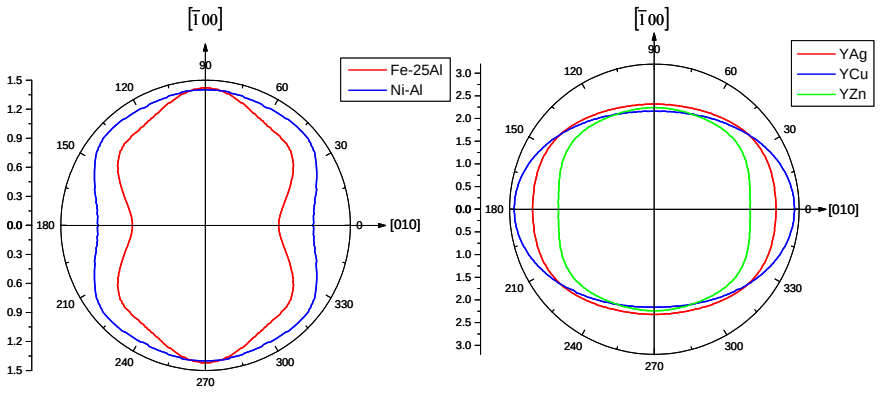
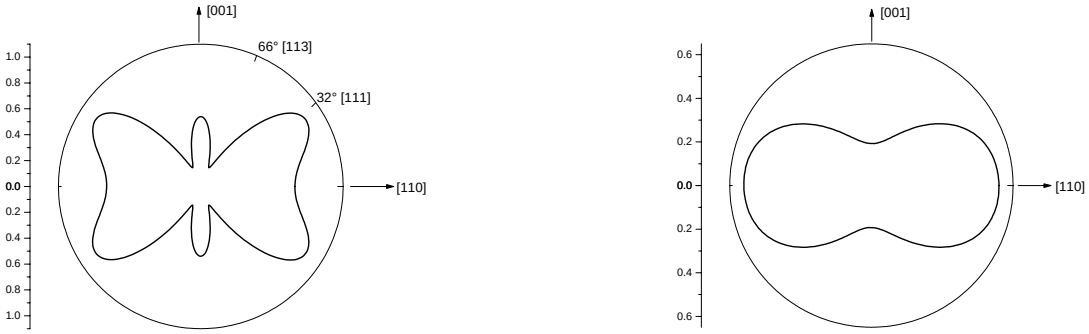


Fig. 1 (1/K) plot for (001)[010] glide loop.

The additional stress to move the dislocations with a kink/bowing part increases with increasing line tension, therefore the glide becomes more difficult for dislocations having larger line tension. Because there is no negative line tension for $(1\,\bar{1}\,0)[110]$ slip system in any of the alloys investigated, the angular variation of the line tension factor values is shown in Fig. 2a for NiAl and Fig. 2b for YCu for this slip system. As can be seen, glide is easier for edge dislocations with kink pairs in YCu than NiAl.



a) **b)**

Fig. 2 Angular variation of line tension factor of $(1\,\bar{1}\,0)[110]$ slip dislocations, a) for NiAl, and b) for YCu.

Impact:

The results clearly show that the ordinary dislocations in YCu, YZn and YAg, in spite of their B2 crystal structure, are intrinsically different than in the B2 Fe-25Al and NiAl intermetallic alloys. The results also provide guidance to the experimental efforts.

Future Work:

The strength of junctions in these systems by using the similar line tension concept will be evaluated.

[1]K. Gschneidner Jr, et. al., *Nature Mat.* **2**, 587, 2003, 2) A.N. Stroh, *Phil. Mag.* **3**, 625, 1958.

Phase Stability, Elastic Constants, and Defect Energetics in Ductile Ordered B2 Compounds

Personnel: J.R. Morris (PI) and Y.Y. Ye (Assistant Scientist)

Scope:

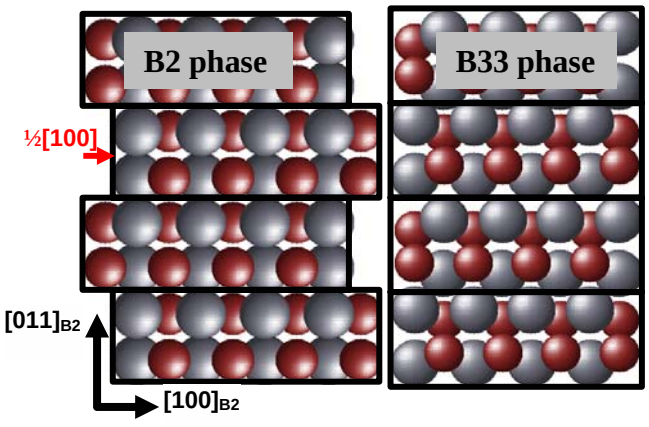
We have used first-principles electronic structure techniques to study the phase stability, elastic constants, and defects in ductile, ordered B2 compounds. Both elastic properties and stacking fault defects on the {110} planes show significant differences from brittle counterparts, in particular NiAl. We have shown that the low defect energies on this plane are related to both the observed <001> slip on this plane, and the close competition between the B2 CsCl structure and the B33 CrB structure.

Research Highlights:

The goal of producing functional intermetallics has a long history, but has been hampered by the limited ductility in many of the materials. The limited ductility has been attributed to the fact that the dominant deformation modes in these materials, the <001> slip modes, do not satisfy the von Mises criterion of five independent slip modes. The presence of <111> slip would satisfy the criterion, but the dislocations often have a high energy. The energy may be reduced if the anti-phase boundary (APB) energy is sufficiently low. This APB energy correlates with the degree of order in these systems, making many ordered B2 compounds brittle.

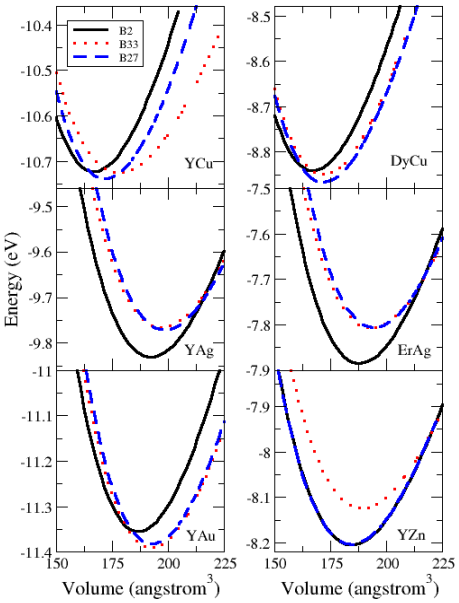
The rare earth B2 (CsCl-type) compounds discovered at the Ames Laboratory exhibit anomalously high ductility. For instance, YAg was found to have a polycrystalline tensile ductility near 27%. Although <111> dislocations were observed, the single crystal properties appear to have deformation behavior similar to that of NiAl, with little or no plasticity when pulled along the <001> directions. Thus, despite the high polycrystalline ductility, the materials do not satisfy the von Mises criterion, confounding the usual understanding.

We have been examining the properties of these materials using first-principles calculations. The calculations provide a non-empirical method of examining the energy and electronic structure of both the pure phases and the defects. In Table 1, we compare the results with experiment, noting that in all cases the theoretical calculations were completed before the experimental results were known. We have also found that the APB energies are quite large (Table 2), consistent with the large degree of order in these systems.



We have also examined stacking faults on the {110} plane, associated with a slip by ½ <001>. This energy is quite low, as shown in Table 2. We have noted that this defect structure is related to the formation of the B33 CrB phase, as shown in the figure above. We believe that this phase stability has an important relationship to the ductility in these systems. Significant ductility has also been reported in Zr(Pd,Ru), ZrCo, and Ni(Ti,Mo) systems, all of which compete closely with the B33 phase.

We have, therefore, examined the phase stability of the B2, B33, and the related B27 phases. The calculations are shown at right. For all systems, the particular rare earth does not make a significant difference (DyCu and YCu are very similar, as are YAg and ErAg). However, while all three phases are close in energy, the competition is dictated by the particular transition metal. For example, YAg is B2 at all temperatures, while YCu transforms to B27 at low temperatures, and YAu is B33. Further study will help determine more specifically how the defects in these materials help determine the ductility.



Impact:

This work has provided direct insight into the bonding and phase stability in these materials. In particular, the calculations of elastic constants demonstrate that these are a new class of ordered intermetallics. The calculations have also provided new insight into the low energy stacking fault defects in these materials.

Future Work:

We will continue calculations on B2 compounds in collaboration with the experimental work. Particular focus is on trends of phase stability and defect energetics in yttrium-containing compounds. We will perform chemical bonding in ordered B2 alloys by *ab initio* calculations through the QUAMBO-based Mulliken overlap population analysis recently developed by our group.

Interactions:

This work is continuing in collaboration with J.R. Morris in the Alloy Behavior and Design project at Oak Ridge National Laboratory.

Table 1. Lattice constant and elastic constants from calculations and from experiment.

	YCu		YAg		YZn	
	Theory	**Exp't**	**Theory**	**Exp't**	**Theory**	**Exp't**
a_0 (angstroms)	3.478	3.476	3.634	3.619	3.572	3.577
Bulk Modulus (MBar)	0.70	0.705	0.686	0.701	0.62	0.642
C_{11} (Mbar)	1.16	1.160	1.05	1.024	0.90	0.997
C_{12} (Mbar)	0.47	0.477	0.50	0.540	0.43	0.465
C_{44} (Mbar)	0.34	0.319	0.37	0.326	0.50	0.473

Table 2. Calculated defect energies in ductile and brittle B2 materials.

defect energies (mJ/m^2)	**YCu**	**YAg**	**YZn**	**NiAl**
1/2 <100> {010} unstable s.f.	700	520	925	1835
1/2 <100> {011} stacking fault	**330**	**315**	**685**	1290
1/2 <111> {110} APB	1030	745	915	815
1/2 <111> {112} APB	1090	680	1375	1050