Title

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Publication Date

1985-07-01

LBL-19947

Presented at the 1985
Conference of the Electron
Microscopy and Analysis Group,
Newcastle upon Tyme, U.K.,
September 2-5, 1985

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July 1985

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for
Advanced
Materials

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Prepared for the U.S. Department of Energy
under Contract DE-AC03-76SF00098

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Accurate Structure Factor Determination of Binary Cubic Solid Solutions

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1. Introduction

The Critical Voltage technique (V_C) in HEED can measure low angle x-ray structure factors of crystalline materials to within 0.1% provided accurate higher angle structure factors and Debye-Waller factors are available (for reviews of the V_C method see e.g., Lally et al., 1972; Thomas et al., 1974). This is far more accurate than simply using structure factors obtained from atomic scattering factors (form factors) determined by Band Structure calculations or x-ray measurements, and by adopting this approach Smart and Humphreys (1978, 1980) have produced complete sets of accurate structure factors for many cubic elements, which they Fourier-analysed to produce finely detailed electron density maps.

Shirley and Fisher (1979) developed a model for the Debye-Waller factors, B, of binary cubic solid solutions. They correlated the variation of B with composition, temperature and short-range order (sro) by the use of two parameters τ and γ which they found could be determined by V_C measurements. Fox (1984) extended this approach and found that both sro and electron charge distribution changes due to alloying in Cu-25 at % Au could be detected by the V_C technique. This method involves obtaining a set of accurate structure factors for the alloy by curve fitting to best pure element form factors and interpolation, and analysing the alloy V_C measurements with an accurate alloy Debye-Waller factor to look for structure factor changes arising from possible electron charge redistribution. This method is an improvement over previous work on this topic which has always considered the form factors of the atoms in the alloy to be essentially the same as those in the pure elements. The extension of this technique to a range of alloys in the systems CuAu, CuAl and FeCr will now be presented.

2. Results and Discussion

CuAu. This solid solution comprises two monovalent metals with a large atomic size difference ($\sim$15%), and which shows an ordering tendency. There has been a great deal of V_C work carried out on this alloy, and the best room temperature B and V_C values necessary for a full analysis are shown in Table 1. Kuroda, et al., (1981) have also investigated the effects of changing sro on the 400 V_C in Cu-15 at % Au, and their results are shown in Table 2.

Table 1 Room temperature B and V_C values for Cu, Au, and their quenched solid solution alloys

$B(Å^2)$	Atomic % Au	V_C^{222}(kV)	V_C^{400}(kV)	V_C^{440}(kV)
$0.54^{(1)}$	0.0	$310 \pm 3^{(1)}$	$605 \pm 3^{(1)}$	$1750 \pm 50^{(2)}$
$0.655^{(5)}$	4.9	$273 \pm 10^{(3)}$	$532 \pm 5^{(3)}$	--
$0.729^{(5)}$	14.9	$<258^{(3)}$	$433 \pm 10^{(3)}$	--
$074^{(6)}$ $0.765^{(4)}$	25.0	$165 \pm 5^{(4)}$	$360 \pm 10^{(4)}$	$1230 \pm 60^{(4)}$
0.51	100.0	--	$108 \pm 2^{(1)}$	$726 \pm 5^{(1)}$

Notes on Table 1: (1) from Thomas et al., (1974); (2) from Rocher and Jouffrey (1972); (3) from Kuroda et al., (1981); (4) from Fox (1984); (5) from present work; (6) from Borie (1957).

In order to analyse the results shown in Tables 1 and 2, the best pure element form factors of Wakoh and Yamashita (1971) for Cu and Doyle and Turner (1968) for Au were used. These were shown to be very accurate by the pure element V_C measurements. The only accurate x-ray Debye-Waller factor available for this system appears to be that of Borie (1957) for a 25 at % Au alloy. This gives $\tau = 1.06$ and $\gamma = 1.12$ in good agreement with theory and with the sro results of Table 2.

It should be noted that sro does not affect the V_C's significantly for the alloy compositions studied in the present work, and has very little effect on the charge redistribution studies if it is ignored. From the V_C results of Table 1 it appears that all the alloy structure factors having (hkl) $\geq$ (200) are the same as those interpolated from the best pure element form factors (within experimental error). The (111) alloy structure factors on the other hand are significantly increased over those interpolated from the best pure element form factors and nearer to the free atom values of Doyle and Turner (1968), as shown in Figure 1. This increase suggests that the electron charge distribution of Cu is made more spherical by gold additions as is its Fermi surface (Coleridge et al., 1984).

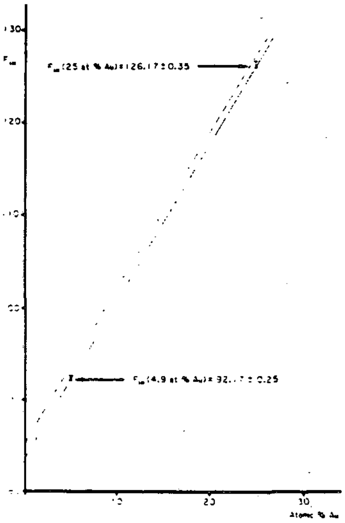

Figure 1. Graph of 111 structure factor, F_{111}, vs. composition for CuAu alloys. Dotted line - Doyle and Turner (1968). Solid line - interpolated between best pure element values. The bars show the experimental results.

Table 2 Changes in room temperature V_C^{400} (for Cu-15 at % Au due to changing sro)

Heat Treatment	sro parameters			V_C^{400}(kv)
	α_1	α_2	α_3	
Furnace cooled from 1073K	--	--	--	438 ± 5
Quenched from 673K	-0.106	0.156	-0.007	433 ± 10
Quenched from 1073K	-0.075	0.135	-0.007	426 ± 10

CuAl In this case monovalent Cu is alloyed with trivalent Al, and the atomic radius disparity is ~6%. These alloys show sro, but it is too small to detect by the V_C method unless the measurement accuracy can be improved to the order of that obtained by Sellar et al (1980). There is only sufficient electron diffraction information to perform a full analysis on one alloy of composition 14.8 at % Al. The best room temperature B and V_C values required are shown in Table 3.

Table 3 Room temperature B and V_C values for Cu, Al, and quenched Cu-14.8 at % Al

B(Å^2)	At % Al	V_C^{222} (kV)	V_C^{400} (kV)
0.54$^{(1)}$	0.0	310 ± 3$^{(1)}$	605 ± 3$^{(1)}$
0.611$^{(2)}$	14.8	332 ± 10$^{(3)}$	641 ± 10$^{(3)}$
0.85$^{(1)}$	100.0	425$^{(1)}$	918 ± 5$^{(1)}$

Notes on Table 3 (1) from Thomas et al., (1974); (2) from Houska and Averbach (1959), (3) from Kuroda et al (1981).

To analyse these results the Cu form factors used were as for CuAu, and for Al the form factors of Inkinen et al., (1970) were found to give best agreement with the V_C measurements. The Debye-Waller factor of Houska and Averbach (1959) appears to be the most accurate available and gives $\tau = 0.97$ and $\gamma = 1.4$. An analysis of these results showed that the alloy low angle structure factors were significantly less than those found by interpolation between best pure element form factors as shown in Table 4. This suggests that not all the Al valence electrons are contributing to the conduction band of the alloy as suggested by Mott (1952) and recently confirmed by Coleridge et al., (1984).

Table 4. Room temperature low-angle x-ray structure factors, F_{hkl}, for Cu-14.8 at % Al

hkl	F_{hkl} (free atom)	F_{hkl} (pure element)	F_{hkl} (experimental)
111	77.89	76.74	76.63 ± 0.15
200	72.07	71.46	71.27 ± 0.15

FeCr This alloy comprises two b.c.c. transition metals of variable valency with an atomic radius difference of 0.6%. These alloys have a segregating tendency, but this is too small to detect by V_C measurements. The best room temperature B and V_C values for the pure elements and three representative alloys are shown in Table 5.

Table 5 Room temperature B and V_C values for Fe, Cr, and three solid solution alloys.

B(Å^2)	At% Cr	V_C^{220} (kV)	V_C^{400} (kV)
0.35 $^{(1)}$	0.0	305 ± 3$^{(2)}$	1278 ± 4
0.323$^{(3)}$	31.9	285 ± 3$^{(3)}$	1275 ± 15$^{(3)}$
0.31 $^{(3)}$	46.0	280 ± 5$^{(3)}$	1275 ± 20$^{(3)}$
0.277$^{(3)}$	75.0	270 ± 3$^{(3)}$	1280 ± 20$^{(3)}$
0.24 $^{(1)}$	100.0	265 ± 3$^{(2)}$	1285 ± 31$^{(1)}$

Notes on Table 5 (1) from Terasaki et al., (1975); from Shirley et al., (1975); (3) from present work.

It can be seen that the V_C^{400} results all agree within experimental error and this immediately suggests that the 200 structure factor is unchanged by alloying. This gives the Debye-Waller factors shown in Table 5 and τ = 0.87. γ could not be determined as the atomic radius disparity is very small. The 110 structure factors are markedly less than those obtained by interpolation between the best pure element form factors of Wakoh and Yamashita (1971) which were used in the analysis as shown in Figure 2. This is to be expected as it is well known that there are significant electronic changes associated with the alloying of Fe and Cr (see e.g., Starke et al., 1962).

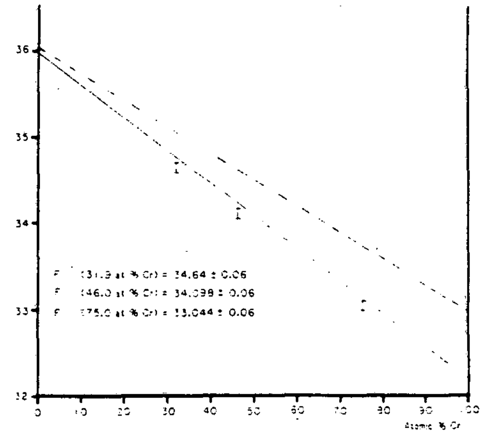

Figure 2. Graph of 110 structure factor, F_{110}, vs. composition for FeCr alloys. Dotted line - Doyle and Turner (1968). Solid line - Interpolated between best pure element values. The bars show the experimental results.

3. Acknowledgments

The authors would like to thank Dr. K.H. Westmacott, National Center for Electron Microscopy, Lawrence Berkeley Laboratory, Berkeley, California for the use of the 1.5 MeV HVEM. This work was supported in part by the U.S. Department of Energy under contract No. DE-AC03-76SF00098.

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