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U. Schwingenschlögl, C. Di Paola, K. Nogita, and C. M. Gourlay

Citation: *Applied Physics Letters* **96**, 061908 (2010); doi: 10.1063/1.3310019

View online: <http://dx.doi.org/10.1063/1.3310019>

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The influence of Ni additions on the relative stability of η and η' Cu_6Sn_5

U. Schwingenschlöggl,^{1,a)} C. Di Paola,¹ K. Nogita,² and C. M. Gourlay³

¹KAUST, PSE Division, Thuwal 23955-6900, Saudi Arabia

²School of Mechanical and Mining Engineering, The University of Queensland, Brisbane 4072, Australia

³Department of Materials, Imperial College, London SW7 2AZ, United Kingdom

(Received 5 January 2010; accepted 18 January 2010; published online 9 February 2010)

We investigate how 5 at. % Ni influences the relative stability of η and η' Cu_6Sn_5 . Synchrotron x-ray diffraction shows that, while Cu_6Sn_5 exists as η' at 25 and 150 °C and transforms to η on heating to 200 °C, $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$ is best fit to η throughout 25–200 °C. Our first principles calculations predict that η' is stable at $T=0$ K in both Cu_6Sn_5 and $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$, but that the energy difference is substantially reduced from 1.21 to 0.90 eV per 22 atom cell by the Ni addition. This effect is attributed to Ni developing distinct bonding to both Cu and Sn in the η phase. © 2010 American Institute of Physics. [doi:10.1063/1.3310019]

A thin layer of Cu_6Sn_5 (~ 5 μm) is integral to micro-electronic solder joints between most Pb-free solders and Cu substrates,¹ and Cu_6Sn_5 is also a candidate material for the anodes of Li-ion batteries.² Four Cu_6Sn_5 phases have been reported, denoted η , η^6 , η^8 , and η' .^{3–5} The highest temperature η phase has a B8-type structure (space group $P6_3/mmc$ with prototype $\text{NiAs-Ni}_2\text{In}$).^{6,7} In the idealized case, this phase consists of a hexagonal sublattice of Sn atoms with Cu atoms occupying all octahedral sites and 20% of trigonal-bipyramidal sites.³ Similar to many B8-type intermetallics, $\eta\text{-Cu}_6\text{Sn}_5$ undergoes superstructure ordering at lower temperature,⁵ accompanied by a distortion of the crystal structure from hexagonal to monoclinic.^{3,5} The η^6 and η^8 phases have space groups $P2_1/c$ and $C2$, respectively, and exhibit ordered occupancy of Cu in trigonal-bipyramidal sites.⁴ The η' phase is the lowest temperature phase, stable at $T < 186$ °C, with space group $C2/c$.³

Ni has significant solubility in Cu_6Sn_5 , occupying Cu sites to form $(\text{Cu},\text{Ni})_6\text{Sn}_5$ with up to ~ 26 at. %Ni.^{8–11} It alters the electrochemical behaviour of Cu_6Sn_5 , opening up the possibility of engineering the anode performance of Li-ion batteries using $(\text{Cu},\text{Ni})_6\text{Sn}_5$.¹² Additionally, $(\text{Cu},\text{Ni})_6\text{Sn}_5$ is the majority intermetallic phase in the reaction layer of solder joints when Sn–Cu–Ni alloys are used as Pb-free solders.^{13–15} There has been recent interest in understanding how Ni influences the relative stability of the η , η^6 , η^8 , and η' phases.^{16–18} Initial experimental results suggest that $(\text{Cu},\text{Ni})_6\text{Sn}_5$ remains as the hexagonal η phase at room temperature after cooling conditions that cause binary Cu_6Sn_5 to transform into the low temperature η' phase.^{16,17} We explore this question by coupling hot-stage powder x-ray diffraction (XRD) experiments with first principles calculations. Although various groups have used first principles calculations to study Cu_6Sn_5 (Refs. 19–21) and $(\text{Cu},\text{Ni})_6\text{Sn}_5$,^{12,22} we apply the approach to examine the influence of Ni on the relative stability of the Cu_6Sn_5 allotropes. We focus on binary Cu_6Sn_5 and $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$ as the latter composition is similar to that reported for the intermetallic layer of solder joints made between Sn–Cu–Ni solders and Cu substrates.^{15,17}

For the experiment, intermetallic phases were obtained by chemical dissolution of Sn from Sn-rich Sn–Cu and Sn–

Cu–Ni alloys. Sn-3 mass % Cu was chosen for Cu_6Sn_5 and Sn-0.7 mass % Cu-0.05 mass % Ni for $(\text{Cu},\text{Ni})_6\text{Sn}_5$, since previous research found the latter to contain Sn and $(\text{Cu},\text{Ni})_6\text{Sn}_5$ with ~ 5 at. %Ni.¹⁸ For both alloys, ~ 30 g of alloy was cast into cups and placed in a solution of 35 g $\text{HOC}_6\text{H}_4\text{NO}_2$ and 50 g NaOH in 1 l of H_2O at 80 °C for 24 h to dissolve the Sn. The resultant intermetallic particles were then pulverized and XRD was conducted at 15 kV in the 2θ range 10° – 60° using a calibrated wavelength of 0.082708 nm. Spectra were recorded at 25, 150, and 200 °C after isothermal holding for 1 h at each temperature. EVA analysis software was used for phase identification and RITAN2000 software for Rietveld analysis.²³

Figure 1 shows the XRD spectra of the two compounds at 25, 150, and 200 °C. In order to magnify any relatively weak superstructure peaks expected of the η^6 , η^8 , and η' phases, the peak heights have been truncated and the 2θ

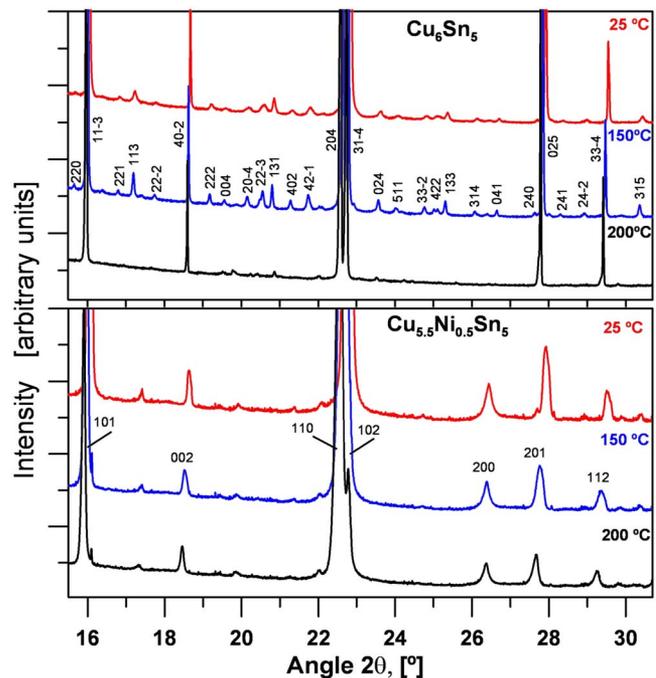


FIG. 1. (Color online) Powder XRD spectra of Cu_6Sn_5 and $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$ at 25, 150, and 200 °C. Cu_6Sn_5 peaks at 150 °C are indexed to η' , and $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$ peaks at 150 °C to η .

^{a)}Electronic address: udo.schwingenschloggl@kaust.edu.sa.

range 15.5° – 30.5° is shown. In Cu_6Sn_5 at 25 and 150°C , small superstructure peaks are clearly evident. Of the four allotropes, these are best fit to the low temperature η' phase, and the 150°C Cu_6Sn_5 peaks are indexed as η' in Fig. 1. On heating to 200°C , most superstructure peaks disappear and the spectra are a better fit to the η phase, suggesting that the η' phase has transformed to η on heating above 186°C , consistent with past research.^{3,19} Note that the 200°C spectra are a relatively poor fit to the η^6 and η^8 phases found by Larsson *et al.*⁴ to be stable at ~ 186 – 350°C .

In $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$, there is no apparent phase transformation since the peaks appear similar at each temperature. Of the four allotropes, each of the $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$ spectra are a best fit to the high temperature η phase, and the 150°C $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$ peaks are indexed as η in Fig. 1. A clear difference between the $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$ and the 200°C Cu_6Sn_5 spectra is the (200) η -peak which is evident at 26.3° in $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$ but absent in Cu_6Sn_5 at 200°C . There are also indications that the $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$ sample is more complex than the η phase since there are additional weak peaks, such as at $2\theta = \sim 17.4^{\circ}$, 19.8° , and 30.3° , that suggest a superstructure may also be present in $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$. Electron diffraction is required to deduce the nature of this possible superstructure.

As in $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$ no phase transformation was detected and the XRD spectra were best fit to the η phase at all temperatures (Fig. 1), the remainder of this letter uses first principles calculations to examine the influence of Ni on the relative stability of the η and η' phases.

Our first principles calculations are based on the generalized gradient approximation, as implemented in the WIEN2K package.²⁴ By its all-electron scheme, band structure data obtained by this full-potential linearized augmented plane-wave code are known to be of high accuracy, which applies both to the relaxation of the crystal structure and the induced relaxation of the electronic states.^{25,26} As we deal with substitutional processes and, thus, have to perform a full structure optimization, this fact is of great importance. In our calculations the charge density is represented by ~ 4000 (η phase, without Ni), ~ 7400 (η phase, with Ni), ~ 19700 (η' phase, without Ni), and ~ 38400 (η' phase, with Ni) plane waves and the \mathbf{k} -mesh for sampling the Brillouin zone comprises 54 (η phase) and 115 (η' phase) points within the irreducible wedge. The Ni $3p$ and Cu $3p$ orbitals are treated as semicore states, whereas the valence states consist of the Ni $3d$, $4s$, Cu $3d$, $4s$, and Sn $4d$, $5s$, $5p$ orbitals. The energy cut-off is determined by $RK_{\text{max}}=7$.

We start from the experimental crystal structures of η - Cu_6Sn_5 (Ref. 17) and η' - Cu_6Sn_5 (Ref. 3) and study the effects of Ni substitution. In the case of the η phase we have to build a supercell consisting of five unit cells stacked along the c -direction to account for the 20% occupancy of the Cu2 site. Therefore, the Cu1 site is split up into three crystallographically inequivalent sites: Cu1a–Cu1c. In the case of the η' phase the XRD results in the four sites Cu1–Cu4. For both phases, we substitute Ni on the different Cu sites to obtain $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$ and perform a full structure optimization. The total energies calculated for the various configurations are summarized in Table I, where the values are given relative to the lowest energy configuration of each phase. We find that Ni substitution is at lowest energy on the Cu2 site in the η phase and the Cu4 site in the η' phase.

TABLE I. Total energy of relaxed η - $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$ and η' - $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$, for Ni substitution at inequivalent Cu sites. Energies are relative to the lowest energy configuration.

	Total energy (eV) η - $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$	Total energy (eV) η' - $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$	
Cu1a	0.54	Cu1	0.12
Cu1b	0.69	Cu2	0.09
Cu1c	0.70	Cu3	0.26
Cu2	0.00	Cu4	0.00

The fact that these two sites are strongly preferred is not surprising since they are characterized by longer Cu–Cu bond lengths which fit better to the optimal Ni–Cu bond length. We give nonoptimized and optimized Ni–Cu, Ni–Sn, Cu–Cu, and Cu–Sn bond lengths of the η and η' phases in Table II. We find that the Ni–Cu bond length is shorter in the η' phase, even though Ni–Cu hybridization and therefore Ni–Cu bonding is stronger in the η phase, see the following discussion. The Ni–Cu bonding results from a destabilization of the Cu–Cu bonds in the first coordination sphere around the Ni atom, which amplifies Cu bonding to the other neighbors. The short Ni–Sn bond length of 2.42 \AA is typical of a Cu2–Sn bond in the η phase and leads to a strong Ni–Sn hybridization which can yield an energy gain when bonding states are created. We note that the 2.42 \AA Ni–Sn bond is not seen in XRD because of the local nature of this distortion.

Comparison of the total energies of the different phases supports the above picture. For Cu_6Sn_5 our calculations show that the η' phase is 1.21 eV per unit cell, i.e., per two formula units, lower in energy than the η phase. This energetic order is maintained after Ni substitution but the energy difference is reduced to 0.90 eV per two formula units for $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$. The η phase thus is not stabilized at $T=0\text{ K}$. However, Ni substitution influences the bonding and strongly reduces the energy difference to the η' phase. In order to understand this behaviour we show in Fig. 2 the Ni density of states (DOS) and compare the Cu DOS of an atom in the clean unit cell to that of an atom next to Ni (with Ni occupying the lowest energy site). We obtain a pronounced dif-

TABLE II. Selected bond lengths of η - $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$ and η' - $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$ before and after the structure optimization.

Bond	η - $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$	η - $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$
	Nonopt. bond length (\AA)	Optimized bond length (\AA)
Ni–Cu	2.73	2.75
Ni–Sn	2.42, 2.54	2.42, 2.66
Cu–Cu	2.54	2.61
Cu–Sn	2.73	2.75, 2.77
Bond	η' - $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$	η' - $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$
	Nonopt. bond length (\AA)	Optimized bond length (\AA)
Ni–Cu	2.64, 2.72	2.67, 2.73
Ni–Sn	2.63, 2.74	2.58, 2.66
Cu–Cu	2.54	2.53
Cu–Sn	2.74, 2.76	2.73, 2.77

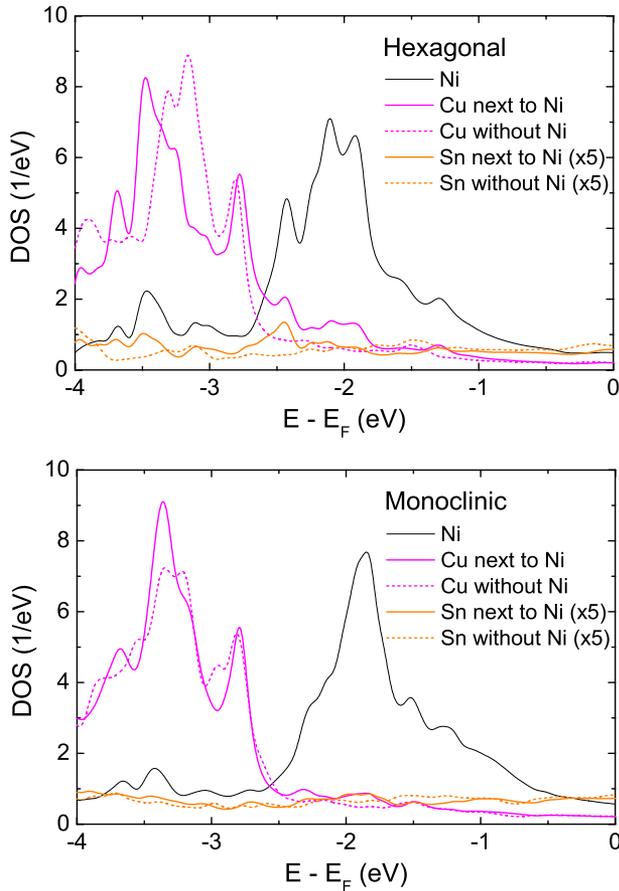


FIG. 2. (Color online) Ni, Cu, and Sn densities of states obtained for the η (hexagonal) and η' (monoclinic) phases of $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$.

ference between the two phases, which nicely explains our observation that under Ni substitution the η phase wins energy relative to the η' phase: In the latter, Ni develops almost no hybridization with any other atom and, therefore, is rather loosely bound. In contrast, in the η phase a distinct bonding to both Cu and Sn is reflected by common DOS peaks at -2.4 , -3.4 , and -3.7 eV. Due to this bonding the system wins energy, relative to the η' phase, when Cu is substituted by Ni.

The narrowing of the relative energy between the η and η' phases at $T=0$ K would reduce the driving force for the η to η' transformation and is consistent with the experimen-

tal finding that this transformation is suppressed in $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$ (Fig. 1). However, it is not clear what the relative stability of the phases is in $\text{Cu}_{5.5}\text{Ni}_{0.5}\text{Sn}_5$ at 298–473 K, and the influence of Ni on the kinetics of any transformation is also expected to be important.

We thank Z.Y. Zhu for helpful discussions. XRD experiments were performed at the Australian Synchrotron (ID:AS091/PD/FI_QLD/1077).

- ¹T. Laurila, V. Vuorinen, and J. Kivilahti, *Mater. Sci. Eng. R.* **49**, 1 (2005).
- ²K. Kepler, J. Vaughey, and M. Thackeray, *Electrochem. Solid-State Lett.* **2**, 307 (1999).
- ³A. K. Larsson, A. Carlsson, L. Stenberg, and S. Lidin, *Acta Crystallogr., Sect. B: Struct. Sci.* **50**, 636 (1994).
- ⁴A. K. Larsson, L. Stenberg, and S. Lidin, *Z. Kristallogr.* **210**, 832 (1995).
- ⁵S. Lidin and A. K. Larsson, *J. Solid State Chem.* **118**, 313 (1995).
- ⁶J. Bernal, *Nature (London)* **122**, 54 (1928).
- ⁷A. Gangulee, G. C. Das, and M. B. Bever, *Metall. Trans.* **4**, 2063 (1973).
- ⁸C. Schmetterer, H. Flandorfer, C. Luef, A. Kodentsov, and H. Ipsier, *J. Electron. Mater.* **38**, 10 (2009).
- ⁹C. Lin, S. Chen, and C. Wang, *J. Electron. Mater.* **31**, 907 (2002).
- ¹⁰C. Li, G. Chiou, and J. Duh, *J. Electron. Mater.* **35**, 343 (2006).
- ¹¹C. M. Gourlay, K. Nogita, J. Read, and A. K. Dahle, *J. Electron. Mater.* **39**, 56 (2010).
- ¹²J. J. Zhang, Y. M. Zhang, X. Zhang, and Y. Xia, *J. Power Sources* **167**, 171 (2007).
- ¹³H. Nishikawa, J. Piao, and T. Takemoto, *J. Electron. Mater.* **35**, 1127 (2006).
- ¹⁴M. Rizvi, C. Bailey, Y. C. Chan, M. N. Islam, and H. Lu, *J. Alloys Compd.* **438**, 122 (2007).
- ¹⁵J. Yoon, Y. H. Lee, D. G. Kim, H. B. Kang, S. J. Suh, C. W. Yang, C. B. Lee, J. M. Jung, C. S. Yoo, and S. B. Jung, *J. Alloys Compd.* **381**, 151 (2004).
- ¹⁶K. Nogita and T. Nishimura, *Scr. Mater.* **59**, 191 (2008).
- ¹⁷K. Nogita, C. M. Gourlay, and T. Nishimura, *JOM* **61**, 45 (2009).
- ¹⁸K. Nogita, *Intermetallics* **18**, 145 (2010).
- ¹⁹G. Ghosh and M. Asta, *J. Mater. Res.* **20**, 3102 (2005).
- ²⁰N. T. S. Lee, V. B. C. Tan, and K. M. Lim, *Appl. Phys. Lett.* **88**, 031913 (2006).
- ²¹J. Chen, Y.-S. Lai, P.-F. Fang, C. Y. Ren, and D.-J. Huang, *J. Mater. Res.* **24**, 2361 (2009).
- ²²C. Yu, J. Liu, H. Lu, P. Li, and J. Chen, *Intermetallics* **15**, 1471 (2007).
- ²³F. Izumi and T. Ikeda, *Mater. Sci. Forum* **321-324**, 198 (2000).
- ²⁴P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Lutz, *Wien2k: An Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties* (Vienna University of Technology, Vienna, 2001).
- ²⁵U. Schwingenschlögl and C. Schuster, *Phys. Rev. Lett.* **102**, 227002 (2009); *Appl. Phys. Lett.* **90**, 192502 (2007).
- ²⁶U. Schwingenschlögl and C. Schuster, *EPL* **86**, 27005 (2009); *Europhys. Lett.* **81**, 26001 (2008).