

January 01, 2006

Anomalous electronic correlations in the ground state momentum density of $\text{Al}_{97}\text{Li}_3$

J. Kwiatkowska

Polish Academy of Sciences, Poland

B. Barbiellini

Northeastern University

S. Kaprzyk

Academy of Mining and Metallurgy AGH, Poland; Northeastern University

A. Bansil

Northeastern University

H. Kawata

High Energy Accelerator Research Organization, Japan

See next page for additional authors

Recommended Citation

Kwiatkowska, J.; Barbiellini, B.; Kaprzyk, S.; Bansil, A.; Kawata, H.; and Shiotani, N., "Anomalous electronic correlations in the ground state momentum density of $\text{Al}_{97}\text{Li}_3$ " (2006). *Physics Faculty Publications*. Paper 29. <http://hdl.handle.net/2047/d20000382>

Author(s)

J. Kwiatkowska, B. Barbiellini, S. Kaprzyk, A. Bansil, H. Kawata, and N. Shiotani

Anomalous electronic correlations in ground state momentum density of $\text{Al}_{97}\text{Li}_3$

J. Kwiatkowska¹, B. Barbiellini², S. Kaprzyk^{2,3}, A. Bansil², H. Kawata⁴ and N. Shiotani⁴

¹*H. Niewodniczański Institute of Nuclear Physics,
Polish Academy of Sciences,
Radzikowskiego 152, 31-342 Kraków, Poland*

²*Department of Physics, Northeastern University,
Boston, MA 02115, USA*

³*Academy of Mining and Metallurgy AGH,
Al. Mickiewicza 30, 30-059 Kraków, Poland*

⁴*Photon Factory, High Energy Accelerator Research Organization,
Tsukuba, Ibaraki 305-0801, Japan*

(Dated: February 6, 2008)

We report high resolution Compton scattering measurements on an $\text{Al}_{97}\text{Li}_3$ disordered alloy single crystal for momentum transfer along the [100], [110] and [111] symmetry directions. The results are interpreted via corresponding KKR-CPA (Korringa-Kohn-Rostoker coherent potential approximation) first principles computations. By comparing spectra for $\text{Al}_{97}\text{Li}_3$ and Al, we show that the momentum density in the alloy differs significantly from the predictions of the conventional Fermi liquid picture and that the ground state of Al is modified anomalously by the addition of Li.

PACS numbers: 71.23.-k, 71.45.Gm, 78.70.Ck, 41.60.Ap, 32.80.Cy

The addition of Li to Al not only reduces the density below that of Al but also increases the elastic modulus. The resulting Al-Li alloy possesses a high strength to weight ratio, which makes it well suited for applications such as fuel efficient aircraft components [1]. Metallurgically, Al is quite 'exclusive' in that only a few percent impurities can be dissolved in Al in the solid solution α phase. For such technological and fundamental reasons, the electronic structure and bonding properties of Al-Li alloys have been the subject of considerable attention over the years [2]. Here we directly probe changes in the electronic ground state of Al due to the presence of Li impurities via Compton scattering measurements. We find that the modifications in the momentum density of Al induced by just a few percent Li atoms are surprisingly large and cannot be accounted for within the standard Fermi liquid type model of the correlated homogeneous electron gas. We show however that the experimentally observed momentum density in $\text{Al}_{97}\text{Li}_3$ can be described reasonably well if correlation effects missing in the standard picture are modeled by promoting 3% electrons in the system from s to p orbitals. Given the increasing current interest in understanding correlation effects in the inhomogeneous electron gas, our results indicate that Al-Li alloys present an example of a simple binary system which exhibits unusual correlation effects even though each of its two constituents is commonly thought of as being a free electron like metal.

Compton scattering [3, 4] is one of the few spectroscopies capable of directly probing the bulk electronic ground state in materials. The measured double-differential cross-section, usually referred to as the Compton profile (CP), is given by

$$J(p_z) = \int \int n(\mathbf{p}) dp_x dp_y, \quad (1)$$

where $n(\mathbf{p})$ is the ground-state electron momentum density. The theoretical analysis of the Compton spectra is often based on the expression of $n(\mathbf{p})$ within the independent particle model [4]. When the right hand side of Eq. 1 is evaluated using the selfconsistent band theory based electron wavefunctions in the local density approximation (LDA), supplemented with electron correlation effects in the homogeneous electron gas, one obtains a fairly sophisticated description of the Compton spectrum. In a randomly disordered alloy, the ensemble averaged momentum density can be obtained within the first-principles KKR-CPA framework [5]. We note two previous high resolution Compton scattering studies of Al-Li [6, 7]. Ref. 6 focuses on the Fermi surface (FS) of $\text{Al}_{97}\text{Li}_3$ and by applying a novel reconstruction technique shows the FS to be in accord with the KKR-CPA predictions. Ref. 7 attempts to examine changes in the CPs with alloying and concludes that within the resolution and statistics of the experiment, the data are consistent with free electron behavior [8].

With regard to experimental details, a single crystal of $\text{Al}_{97}\text{Li}_3$ alloy was grown by Bridgman method. The starting material was an alloy made from high purity Al (99.999%) and Li (99.95%), containing excess of Li above the desired composition to allow for losses. The load was kept under 3 atm. Ar pressure during the process of crystallization. The final Li content in the alloy single crystal was determined by Atomic Absorption Spectrometry to be 3 at.%. The Li content was also checked independently using Proton Induced Gamma Emission. The crystal was oriented using Laue X-ray diffraction method and disc-shaped samples, 10mm in diameter and 1.5mm thick, were cut parallel to the (100), (110), and (111) crystallographic planes. The CPs were measured with the high resolution Compton spectrometer installed at

the KEK-AR synchrotron [9]. The incident energy of photons was 60 keV, the scattering angle 160° , and the momentum resolution of the experiment is estimated to be 0.12 a.u. The total number of accumulated counts under each directional profile was about 10^8 . The valence profiles of Al used for comparison were measured by Ohata *et al.* [10] under the experimental conditions of the present measurements. However, we remeasured the [110] CPs of Al and $\text{Al}_{97}\text{Li}_3$ in the same experimental run in order to independently check the validity of the changes in the CPs with alloying discussed in this article.

Concerning computational details, selfconsistent electronic structures were first obtained in $\text{Al}_{1-x}\text{Li}_x$ at $x = 0$ and $x = 0.03$, respectively, using the KKR-LDA-CPA scheme. The total energy was not minimized, but instead the experimental lattice constant $a = 7.6534$ a.u. for Al was used for both Al and the 3% alloy. These results provided the input for evaluating the 3D momentum density $n(\mathbf{p})$ in terms of the momentum matrix element of the KKR-CPA Green's function and the CPs for momentum transfer along the three high symmetry directions. The CPs for the limiting case of $x = 0$ are in good accord with those obtained independently in Al via the KKR approach. The details of the KKR-LDA-CPA methodology and the associated momentum density and CP computations are described in Ref. [5]. The accuracy of the theoretical CPs is estimated to be 1 part in 10^4 so that changes in the CPs between Al and the 3% Li alloy could be evaluated reliably.

Fig. 1 considers measured and computed changes

$$\Delta J_{\mathbf{q}}(p_z) = J_{\mathbf{q}}(p_z)_{\text{Al}} - J_{\mathbf{q}}(p_z)_{\text{Al}_{97}\text{Li}_3}, \quad (2)$$

in the valence CP of Al for momentum transfer p_z along the three principal symmetry directions when 3% Li is added. $\Delta J_{\mathbf{q}}(p_z)$ is a useful quantity because it allows us to focus on the properties of only those electrons which are affected significantly by alloying. We can obtain a handle on the size of $\Delta J_{\mathbf{q}}(p_z)$ by assuming all valence electrons to be free electron like. The momentum density $n(\mathbf{p})$ is then uniform within the Fermi sphere of radius p_F and the corresponding CP is given by the simple parabolic form $J_{\mathbf{q}}(p_z) = V_{WS}/(4\pi^2)(p_F^2 - p_z^2)\Theta(p_F - p_z)$, where V_{WS} is the Wigner-Seitz cell volume and Θ is the step function. The addition of 3 % Li to Al causes a decrease of 0.06 valence electrons/atom and a concomitant decrease in p_F from 0.929 a.u. in Al to 0.919 a.u. in $\text{Al}_{97}\text{Li}_3$. The use of these p_F values yields the isotropic free electron result for $\Delta J_{\mathbf{q}}$ in Fig. 1 (dashed lines), with a value of ≈ 0.03 extending to $p_z \approx 1$ a.u., which is representative of the scale of the experimentally observed changes $\Delta J_{\mathbf{q}}(p_z)$.

The KKR-CPA curves in Fig. 1 (red solid lines) are based on a realistic description of the electronic structures of both Al and $\text{Al}_{97}\text{Li}_3$ and display fine structure which reflects modifications of the free electron wavefunctions due to solid state effects. Nevertheless, it is striking

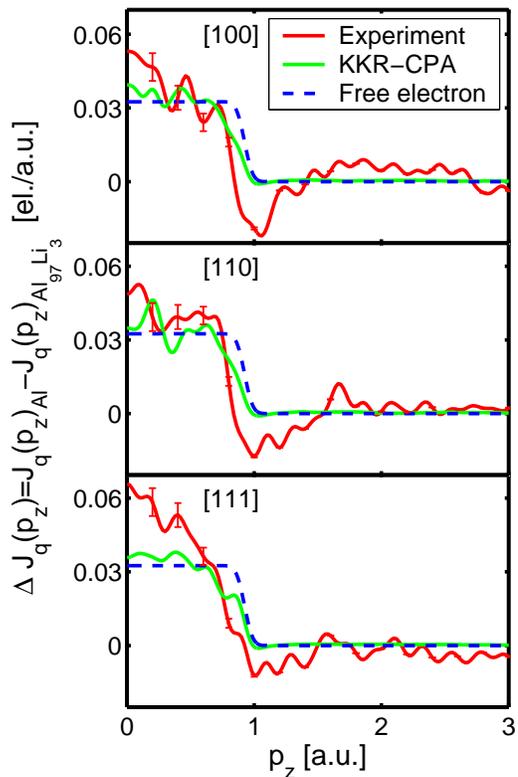


FIG. 1: Experimentally observed changes $\Delta J_{\mathbf{q}}(p_z)$ (Eq. 2) between the valence [100], [110] and [111] CPs of Al and $\text{Al}_{97}\text{Li}_3$ are compared with the corresponding results for the free-electron model and the KKR-CPA theory.

that the KKR-CPA prediction differs significantly from the experimental results. This discrepancy is particularly noteworthy at and around the Fermi momentum of ≈ 1 a.u. where the error bars on the experimental data are quite small. The data show a substantial negative excursion starting around ≈ 0.8 a.u. and non-zero values extending to high momenta. In sharp contrast, the KKR-CPA yields changes $\Delta J_{\mathbf{q}}(p_z)$, which are essentially zero beyond ≈ 1 a.u. and positive in sign at all momenta. We have carried out extensive additional computations of the CP in a variety of ordered Al-Li crystal structures in order to ascertain if the aforementioned discrepancies in $\Delta J_{\mathbf{q}}$ may be related to clustering or ordering effects in the alloy which are missing in the KKR-CPA single site framework. In this connection, CPs were computed in Al_3Li and Al_2Li_2 , but the $\Delta J_{\mathbf{q}}$'s so determined were similar to the KKR-CPA curves in all cases and in particular did not show a non-zero value for momenta greater than ≈ 1 a.u. It is clear that the discrepancies between theory and experiment in Fig. 1 cannot be understood within the conventional LDA-based picture of the changes in the electronic spectrum of Al induced by the addition of a few percent Li impurities and indicate a failure of this picture at a fundamental level.

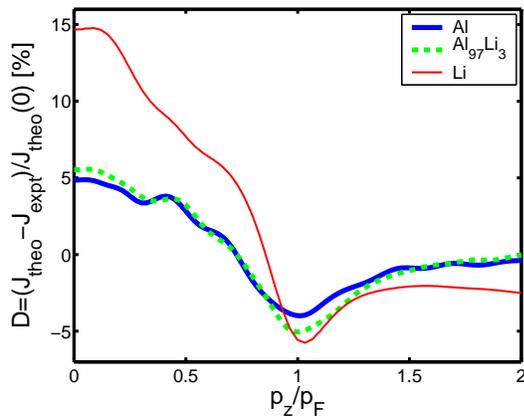


FIG. 2: Normalized differences between the LDA-based theoretical Compton profiles (J_{theo}) and the corresponding experimental profiles (J_{expt}) along the [100] direction in Li, Al and $\text{Al}_{97}\text{Li}_3$ as a function of the scaled momentum p_z/p_F , where p_F is the Fermi momentum in various cases.

Fig. 2 further explores how the description of the ground state momentum density provided by the LDA breaks down in Al, Li and $\text{Al}_{97}\text{Li}_3$. Here the normalized deviation $D = (J_{theo} - J_{expt})/J_{theo}(0)$ between the theoretical and experimental CPs is considered (in percent) as a function of p_z in units of p_F . In this way, the extent to which electron correlation effects beyond the LDA are at play in different systems can be identified and compared on a common scale. Although Fig. 2 compares the CPs along the the [100] direction, results for other directional CPs are similar and are not shown for brevity. The deviations in Al (thick blue line) can be understood in terms of the Fermi liquid model where the break Z_F in the momentum density at the Fermi energy, which is implicitly set equal to unity in the band theory calculations, is renormalized to a value of $0.7 - 0.8$ in line with the expected values in the correlated electron gas [11]. On the other hand, deviations in Li (thin red line) are seen to vary from +15% at $p_z = 0$ to -6% around p_F and are much larger than in Al [12]. The behavior of the momentum density of Li near the Fermi momentum has been investigated extensively in terms of CP experiments to adduce an effective Z_F value of nearly zero [13], which is quite far from the corresponding electron gas predictions of 0.65-0.75 [14]. Turning to $\text{Al}_{97}\text{Li}_3$ in Fig. 2, we see that the D -values in the alloy (dashed line) and Al differ by only a few percent at most momenta, but around the Fermi momentum, D -values in the alloy are comparable to those in Li. In other words, just a few percent Li atoms induce large changes in the electronic states of Al in a highly non-LDA like manner. The anomalous effects in the momentum density are seen to extend in the alloy over a substantial momentum range of $0.9 \leq p_z/p_F \leq 1.4$ a.u. These observations are consistent with our earlier

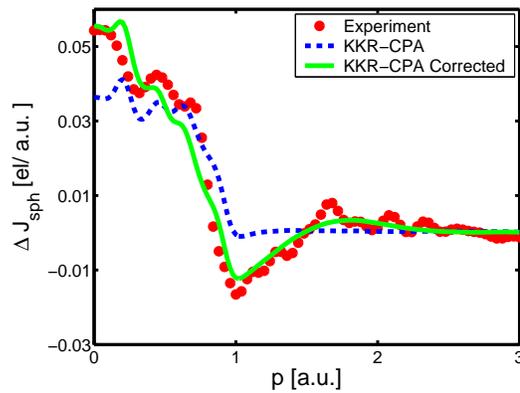


FIG. 3: Spherical average ΔJ_{sph} of the experimental $\Delta J_{\mathbf{q}}$ considered in Fig.1 is compared with the corresponding KKR-CPA result with and without the correction $C(p)$ of Eq. 4.

discussion on Fig. 2 which also pointed to the presence of unusual discrepancies in $\Delta J_{\mathbf{q}}$ around p_F .

In order to gain insight into the nature of discrepancy depicted in Fig. 1, we consider the spherical average ΔJ_{sph} of the change $\Delta J_{\mathbf{q}}$ in the valence CP of Al due to alloying, which has been discussed previously in connection with Fig. 1 above [15]. ΔJ_{sph} can be obtained in a cubic system via [10]

$$\Delta J_{sph} = (10\Delta J_{[100]} + 16\Delta J_{[110]} + 9\Delta J_{[111]})/35. \quad (3)$$

Fig. 3 presents results for ΔJ_{sph} . As expected from the discussion of Figs. 1 and 2 above, the theoretical KKR-CPA curve (dashed line) differs substantially from the experimental data. The key to understanding this discrepancy in Fig. 3 is to recognize that correlation effects can be viewed as exciting some electrons into higher energy unoccupied levels as a way of modifying the character of the ground state wavefunction. The lowest unoccupied orbitals in Li and Al are the $2p$ and the $3p$ orbitals, respectively. It is natural therefore to consider the effect of promoting an electron from an s to a p orbital. The resulting change in the CP is straightforwardly shown to be:

$$C(p) = w \left(\left| \int R_0(r) j_0(pr) r^2 dr \right|^2 - \left| \int R_1(r) j_1(pr) r^2 dr \right|^2 \right), \quad (4)$$

where w is a weighting factor, j_ℓ are spherical Bessel functions, $R_\ell(r)$ are the radial wavefunctions in the crystal, and ℓ is the angular momentum index. The radial integrals extend to the Wigner-Seitz sphere radius R_{WS} . Specifically, we used Al $3s$ and $3p$ radial wavefunctions in evaluating the right side of Eq. 4, but the shape of $C(p)$ is found to be essentially the same if Li $2s$ and $2p$ wavefunctions are used instead [16].

Fig. 3 shows the result of correcting KKR-CPA via the term $C(p)$ where the weight factor w of Eq. 4 has

been used as a fitting parameter to adjust the overall size of the correction term. A good fit is obtained for $w = 0.03/\text{electron}$ (solid green line). We emphasize that the deviations in the momentum density of pure Al compared to the LDA predictions, which were discussed above in connection with Fig. 2, can be explained reasonably within the 'standard' electron gas picture. Such standard correlation effects will of course also be present in $\text{Al}_{97}\text{Li}_3$ with a magnitude similar to that of Al because the electron density in Al and $\text{Al}_{97}\text{Li}_3$ is nearly the same with the p_F values differing by only about 1%. Therefore, when the difference $\Delta J_{\mathbf{q}}$ is formed in Eq. 2, we would expect such standard electron gas type correlation effects to be cancelled. In other words, $w = 0.03/\text{electron}$ represents an *additional* correlation effect induced by the introduction of Li impurities in Al and implies that about 3% valence electrons in $\text{Al}_{97}\text{Li}_3$ need to be promoted from $s-$ to $p-$ like states to account for the observed momentum density change in $\text{Al}_{97}\text{Li}_3$. We may look upon this result as indicating that correlations and the associated changes in the effective potentials produce an enhanced p character of the ground state wave function of $\text{Al}_{97}\text{Li}_3$. Note that since only 1% of valence electrons in $\text{Al}_{97}\text{Li}_3$ come from Li atoms, the weight w of 3% cannot be explained in terms of Li electrons alone and indicates a significant involvement of Al electrons near the Li impurities in generating anomalous changes in the momentum density of the alloy.

In conclusion, our study provides direct evidence that the electronic ground state of Al is modified anomalously by the addition of Li impurities. The experimental momentum density in $\text{Al}_{97}\text{Li}_3$ is found to differ significantly from the predictions of the conventional Fermi-liquid type picture where correlation effects are included within the framework of the homogeneous electron gas. We show that the observed anomaly in the momentum density of the alloy can be accounted for if 3% electrons in $\text{Al}_{97}\text{Li}_3$ are transferred from $s-$ to $p-$ like orbitals so that the p character of the ground state wavefunction becomes enhanced. It is clear that Li impurities in Al constitute a relatively simple exemplar system in which the standard treatment of the interacting electron gas breaks down and

properties of the correlated *inhomogeneous* electron gas must be considered.

We thank Franek Maniawski for help with growing the single crystal of $\text{Al}_{97}\text{Li}_3$. This work was supported by the U.S.D.O.E. contract DE-AC03-76SF00098, by the Polish Committee for Scientific Research, Grant Number 2 P03B 028 14 and benefited from the allocation of super-computer time at NERSC and the Northeastern University's Advanced Scientific Computation Center (ASCC). This work was carried out with the approval of the Photon Factory Advisory Committee, Proposal No. 97G288.

-
- [1] J.W. Martin, Ann. Rev. of Mat. Sci. **18**, 101 (1988).
 - [2] See e.g. A. Van der Ven and G. Ceder, Phys. Rev. Lett. **94**, 045901 (2005).
 - [3] M.J. Cooper *et al.* in *X-Ray Compton Scattering*, Oxford University Press (2004).
 - [4] I.G. Kaplan *et al.*, Phys. Rev. B **68**, 235104 (2003).
 - [5] A. Bansil *et al.*, J. Phys. Chem. Solids **62**, 2191 (2001).
 - [6] I. Matsumoto *et al.*, Phys. Rev. B **64**, 045121 (2001).
 - [7] P. Suortti *et al.*, J. Phys. Chem. Solids **62**, 2223 (2001).
 - [8] I. Matsumoto *et al.*, J. Phys. Chem. Solids **61**, 375 (2000) discuss a preliminary study of the [111] CP in $\text{Al}_{97}\text{Li}_3$.
 - [9] Y. Sakurai *et al.*, Rev. Sci. Instr. **63**, 1190 (1992).
 - [10] T. Ohata *et al.*, Phys. Rev. B **62**, 16528 (2000).
 - [11] This is commonly referred to as the Lam-Platzman correction where the momentum density obtained within the independent particle framework of the band theory is corrected by using the momentum density of the correlated homogeneous electron gas [12].
 - [12] B. Barbiellini, A. Bansil, J. Phys. Chem. Solids **62**, 2181 (2001).
 - [13] W. Schülke *et al.*, Phys. Rev. B **54**, 14381 (1996).
 - [14] Momentum density of Li cannot thus be understood within the framework of correlated homogeneous electron gas. Ref. [12] considers the importance of the correlated *inhomogeneous* electron gas in this connection.
 - [15] There are of course smaller anisotropic effects seen in Fig. 3, but their quantitative nature is uncertain and we will not be concerned with these effects here.
 - [16] The radial wavefunctions in the crystal of course depend on energy. In evaluating $C(p)$ we used wavefunctions at the Fermi energy, although computations at other energies yielded little change in the shape of $C(p)$.