Electronic Structure of Copper Antimony Using Compton Scattering Technique

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Abstract:

In this paper we present the first ever measured experimental electron momentum density of Cu_2Sb at an intermediate resolution (0.6 a.u.) using 59.54 keV ^{241}Am Compton spectrometer. The measurements are compared with the theoretical Compton profiles using density function theory (DFT) within a linear combination of an atomic orbitals (LCAO) method. In DFT calculation, Perdew-Burke-Ernzerhof (PBE) scheme is employed to treat correlation whereas exchange is included by following the Becke scheme. It is seen that various approximations within LCAO-DFT show relatively better agreement with the experimental Compton data. Ionic model calculations for a number of configurations $(Cu^{+x/2})_2(Sb^{-x})$ $(0.0 \le x \le 2.0)$ are also performed utilizing free atom profiles, the ionic model suggests transfer of 2.0 electrons per Cu atom from 4s state to 5p state of Sb.

Key words: electron Momentum Density, Compton Profile, LCAO Method, Ionic Model, charge Transfer.

Introduction:

Copper Antimony (Cu_2Sb) crystallizes in a tetragonal system structure space group (P4/nmm), No 129 with two formula units per unit cell. The unit cell parameters are a = 3.97 ˚A and c = 6.06 A˚, the Cu atoms are situated at (0.75 0.25 0.0) and (0.25 0.25 0.27) and Sb atom at (0.25 0.25 0.7) positions crystallizes. Copper Antimony is considered nowadays as one of the most Intermetallic compounds in modern technology, it presents an attractive alternative to graphite as anode materials in Li ion insertion batteries due to a particular to the high capacity, an acceptable rate capability and operating potentials well above the potential of metallic lithium[1]. Ren et al. [2] attempt a novel process to prepare nanoscale Cu_2Sb and alloy powders as anode materials for lithium ion batteries. The nanoscale Cu_2Sb alloy shows a good cyclability with a stable specific capacity of 200 mA/h g−1 within 25 cycles. Mosby and Prieto [3] describe the direct single potential electrode position of crystalline Cu_2Sb as a promising anode material for lithium ion batteries. Sharma et al. [4] study the mechanism of lithium insertion/intercalation in the anode materials InSb and Cu_2Sb using first principle total energy calculations. Morcrette et al. [5] have demonstrated that Cu_2Sb electrodes can operate reversibly in lithium cells and demonstrated that the structural reversibility of the Cu_2Sb electrode can be obtained in two special cases first when the particle size of Cu_2Sb is small and when the powders are ball milled with carbon and second when Li_2CuSb is used as the starting material and some Sb is lost from the electrode during charge. R. K. Rajgarhia et al[6] study that the microstructural stability of copper with antimony dopants at grain boundaries. L.M.L. Fransson el al [7] study the phase transitions is lithiated of Cu_2Sb anodes for lithium batteries.

Compton scattering, which is an inelastic scattering of X-rays from electrons at large energy and momentum transfer, is a unique probe to study the ground-state electron momentum densities [8]. This technique is insensitive to crystal defects. The quantity measured in such experiments known as Compton profile, J(pz), is the projection momentum density $\rho(\overrightarrow{p})$ on the along the scattering vector (usually z-axis of a Cartesian coordinate system). It is defined as

$$J(pz) = \iint \rho(\vec{\mathbf{p}})dp_z dp_y \quad \ldots (1)$$

An electron with momentum component p_z along the scattering vector shifts the scattered photon energy from E_1 to E_2, where

$$\frac{p_z}{m_o c} = \frac{\{E_2 - E_1 + E_1E_2(1-\cos\emptyset)/E_O C^2\}}{\{E_1^2 + E_2^2 - 2E_1E_2\cos\emptyset)^{1/2}} \ldots (2)$$

Here Ø is the photon scattering angle. In crystalline materials, Compton data are mainly interpreted in terms of the difference between the pairs directional profiles, i.e.

$$\Delta J(P_Z) = J_{hkl}(P_Z) - J_{h'k'l'}(P_Z) \ldots (3)$$

Where hkl and $h'k'l'$denote planes perpendicular to the scattering vector. In this paper, unless stated, all quantities are in atomic units (a.u.) where e=ħ=m=1 and c=137.036, giving unit momentum=1.9929×10^{-24} $Kgms^{-1}$, unit energy=27.212 eV and unit length=5.2918×10^{-11}m.

Experimental:

1- Synthesis of Cu_2Sb

Cu_2Sb powders are synthesized by mixing Cu and Sb in a 2:1 ratio and placed in a quartz tube sealed under argon and heated to 500 °C during 1 week. The phase purity and crystal structure of sample was analyzed by Philips X'pert Pro X-Ray diffractometer having CuKα (λ=1.5460Å) source of X-rays, is shown in Fig.1

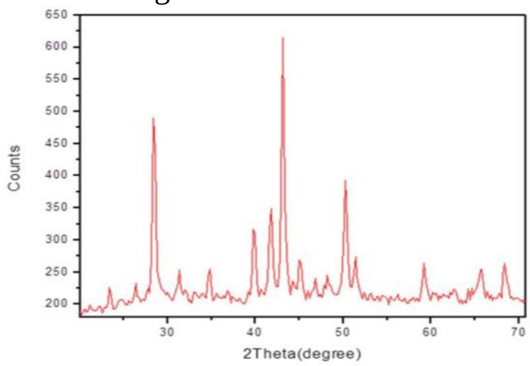

Fig.1. XRD Patterns of Cu_2Sb of Different Size

2- Compton Profile Measurements

The ^{241}Am gamma-ray spectrometer described by Sharma-et al. [9] has been employed for the Compton profile measurements. The incident gamma rays of 59.54KeV from 5 Ci annular ^{241}Am source are scattered at a angle $166^o\pm3.0^o$ by the sample of Cu_2Sb. The scattering chamber is evacuated to about 10^{-2} Torr with a rotary oil pomp to reduce the contribution of air scattering and the sample is held vertical by affixing on the back of the lead covered brass slab with a hole of radius 9.05mm. The scattered radiation is analyzed by using an HPGe detector (Canberra model, GL110S), which is cooled with liquid nitrogen providing overall momentum resolutionn0.6 a.u. The spectra are recorded by using a multichannel analyzer (MCA) with 4096 channels. The channel width was~ 20 eV, corresponding to 0.03 a.u. of momentum. To correct for the background, measurement with the empty sample holder is performed for 11 h and the measured background is subtracted from the raw data channel by channel after scaling it to the actual counting time. Thereafter the corrected background spectra are processed for several corrections like instrumental resolution, sample absorption and scattering cross section using computer code of the Warwick group [10, 11] to obtain the Compton profile. After converting the profiles to the momentum scale, a Monte Carlo simulation is performed to account for multiple scattering corrections history of approximately 10^7 photons were considered. The effect of multiple scattering is found to be %4.6174 in the range -10 a.u. to +10 a.u. The correction profile is normalized to 44.881 electrons, in the range 0 to +7 a. u.

3- Computation Details, DFT-LCAO Calculation

To compute the theoretical Compton profile, the LCAO method embodies in CRYSTAL06 code [12] of Torino group has been used. In this method each crystalline orbital $\psi_i(\mathbf{r.k})$ is a linear combination of Bloch functions $\varphi_\mu(\mathbf{r.k})$ defined in terms of local function $\varphi_\mu(\mathbf{r})$ normally referred as atomic. The local functions are expressed as linear combination of certain number of individually normalized Gaussian type function .The Kohn-Sham Hamiltonian is constructed while considering the exchange functional of Becke [13] and Perdew-Burke-Ernzerhof (PBE) correction functional [14,15].

4- Ionic Model

The theoretical Compton profile of Cu_2Sb for different ionic configurations is calculated from the free atom profile of Cu_2 and Sb as taken from Bigge et al. [16]. The valence profile for various $(Cu^{+x/2})_2(Sb^{-x})(0.0\leq x \leq 0.2$ in step of 0.5) configurations is calculated by transferring x electrons from the 4S shell of Ca to the 5P shell of Sb . the valence profile for $(Cu^{+x/2})_2(Sb^{-x})$, configurations is added to the core contributions to get the total profile . All the profile are then appropriately normalized to compare with other calculations and the measurement.

Results and Discussion:

In the Table 1, we have listed the numerical values of experimental Compton profile along with the unconvoluted spherically averaged theoretical Compton profile (LCAO-DFT)of Cu_2Sb. The Ionic profile, derived from the free atom model considering various ionic arrangements i.e $(Cu^{+x/2})_2(Sb^{-x})(0.0\leq x \leq 0.2$) , are also included in the Table 1.

Table-1:- Unconvoluted Theoretical (DFT-LCAO and Ionic) and the Experimental Compton Profiles of C u$_2$Sb.All Profile are Normalized to 44.881 Electrons in the Range 0 to +7 a,u. Statistical Errors (±σ) are Also Given at Some Points.

p_z(a.u.)	$J(p_z)$ in e/a.u.					
	DFT-LCAO	Ionic model				Experiment
		$(Cu^{+0.25})_2(Sb^{-0.5})$	$(Cu^{+5.0})_2(Sb^{-1.0})$	$(Cu^{+0.75})_2(Sb^{-1.5})$	$(Cu^{+1.0})_2(Sb^{-2.0})$	
0	18.141	22.529	21.635	20.689	19.687	18.803±0.073
0.1	18.204	22.330	21.572	20.770	19.920	18.815
0.2	18.182	21.837	21.393	20.923	20.426	18.617
0.3	17.856	20.136	20.014	19.885	19.749	18.119
0.4	17.448	18.403	18.495	18.592	18.696	17.387
0.5	16.938	16.909	17.093	17.288	17.495	16.593
0.6	16.337	15.714	15.908	16.115	16.333	15.852
0.7	15.681	14.780	14.948	15.126	15.314	15.138
0.8	15.010	14.251	14.382	14.521	14.668	14.389
1	13.746	13.058	13.131	13.209	13.291	12.950±0.059
1.2	12.658	12.156	12.201	12.249	12.300	11.969
1.4	11.701	11.321	11.356	11.393	11.433	11.012
1.6	10.801	10.443	10.475	10.510	10.546	10.244
1.8	9.939	9.572	9.603	9.636	9.671	09.664
2	9.117	8.849	8.878	8.910	8.944	08.712±0.047
3	5.670	5.462	5.479	5.498	5.518	5.225±0.033
4	3.533	3.403	3.411	3.420	3.430	3.261±0.024
5	2.488	2.440	2.444	2.449	2.454	2.383±0.019
6	1.891	1.869	1.871	1.874	1.876	1.960±0.015
7	1.502	1.460	1.461	1.462	1.464	1.438±0.011

for a quantitative comparison of the theory and experiment, difference profiles $\Delta J=J^{Theory}(p_z)- J^{Expt}(p_z)$ have been deduced after convoluting all theoretical profile, with a Gaussian function of 0.6 a.u. FWHM. All values are normalized to 44.881 electrons within 0 to +7 a.u. range of momentum. These differences (ΔJ), exhibiting the difference between convoluted theory and experiment have been plotted in the Fig. 2.This figure depicts that the effect of charge transfer from Cu to Sb is largely visible within 0.0 to 2.0 a.u. rang of momentum and the ionic configuration with x=0.5 shows the largest deviation with the experiment around J(0). The best agreement is found for x=2. Beyond 2.0 a.u., all configurations show identical behavior and the profiles are overlapping with each other. Such an agreement beyond 2.0 a.u., is expected because the contribution is this momentum range is mostly due to inner electrons, which remain unaffected in the formation of compound. On the basis of χ^2 checks , and as is obvious from Fig.2, also, it is found that $(Cu^{+1})_2$ (Sb^{-2})configuration gives the best agreement among the ionic arrangements suggesting transfer of 2 electrons from the valence 4s state of Cu atom to the 5p states of Sb atoms.

To examine the directional features theoretically, we consider the directional Compton profiles of Cu_2Sb along the [100], [110] and [001] directions. All profiles are convoluted by a Gaussian function of 0.6 a.u. FWHM, before deriving this anisotropies in fig.3. The figure depicts that the anisotropies [100]-[110] is positive in nature but [110]-[001] and [100]-[001] are negative around at p_z=0.0 a.u. It indicates larger occupied states along [100] direction with low momentum. A close inspection of this figure reveals that maximum anisotropy is seen between [100] and [110] directions at 1a.u. All anisotropies are visible up to 2.0 a.u. Measurements on single crystalline samples of Cu_2Sb would be helpful to examine the directional features of bonding through anisotropies.

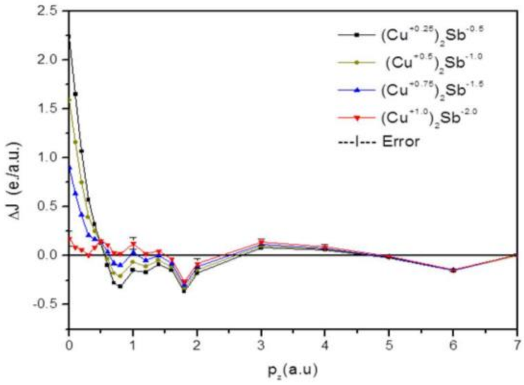

Fig.2. Difference (ΔJ) between Convoluted Ionic and Experimental Compton Profiles of Cu_2Sb. Experimental Errors (±Σ) are Also Shown at Points. All Ionic Profile are Convoluted with the Gaussian of 0.6 A.U. FWHM.

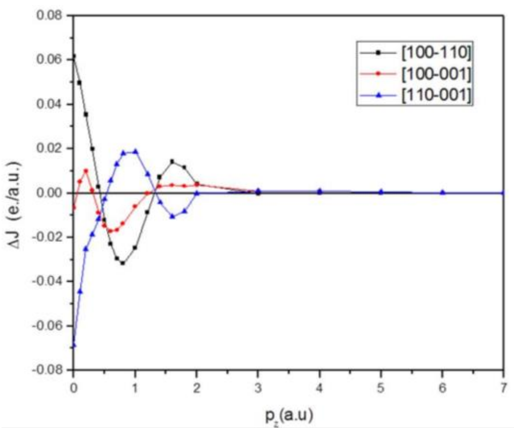

Fig.3. Directional Anisotropies, $\Delta J(p_z)$, for Cu_2Sb for the Pair of Directions [100]–[110], [100]–[001] and [110]–[001].

Next in Fig. 4, we compare the total experimental and DFT-PBE scheme based Compton profiles. The difference ($\Delta J = J^{Theory}(p_z) - J^{Expt}(p_z)$) between two data also presented in the inset of the figure. The figure indicates that DFT-PBE scheme underestimates the electron momentum density in the momentum range $0.0<p_z<0.5$ a.u. while the trend reversed in the momentum range $0.5<p_z<2.0$ a.u. The difference between two data is negligible in the high momentum region because the contribution in this region is mostly due to core electrons, which remain unaffected in the solid formation.

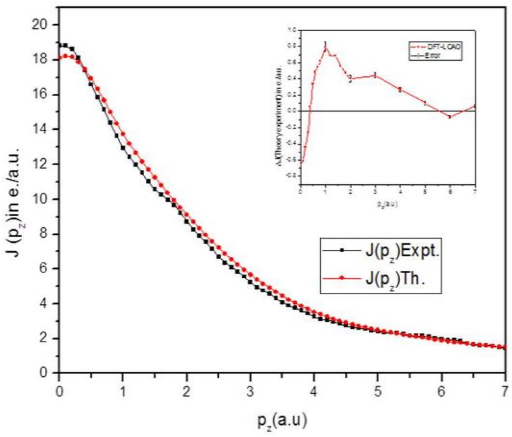

Fig.4. The Absolute DFT-LCAO and Experimental Compton Profiles of Cu_2sb. Inset Shows the Difference Between Two Data. Both Profiles are Convoluted with the Gaussian of 0.6 a.u. FHWM.

Conclusions:

Experimental Compton profile (CP) of polycrystalline Cu_2Sb. is measured at an intermediate resolution of 0.6 a.u. The experimental profile is compared with the theoretically computed Compton profile (CP) using DFT scheme of LCAO approach. It is seen that various approximations within LCAO-DFT show relatively better agreement with the experimental Compton data . The anisotropies in momentum densities depict larger occupied states along [100] direction with low momentum. In addition, the

Ionic model has also used different amount of charge transfer from Cu to Sb atom. The ionic model supports a transfer of 2 electrons from 4s state of Cu atom to 5p state of Sb atoms.

References:

[1] Reshaka, A. H. and Kamarudinb, H. 2011. Theoretical investigation for Li_2CuSb as multifunctional materials: Electrode for high capacity rechargeable batteries and novel materials for second harmonic generation, J. Alloys and Compounds, 509(30): 7861– 7869.

[2] Ren, J.; He, X.; Pu, X.; Jiang, C. and Wan, C., 2006. Chemical reduction of nano-scale Cu_2Sb powders as anode materials for Li-ion batteries, Electrochim. Acta, 52(4): 1538–1541.

[3] Mosby, J.M.; Prieto, A, L. and Am, J., 2008. Direct electrodeposition of Cu2Sb for lithium-ion battery anodes. Chem. Soc. 130(32): 10656–10661.

[4] Sharma, S.; Dewhurst, J. K and Ambrosch-Draxl, C.2004. Lithiation of InSb and Cu2Sb:A theoretical investigation, Phys. Rev. B 70 (10) : 104110.

[5] Morcrette, M.; Larcher, D.; Tarascon, J. M.; Edstrom, K.; Vaughey and Thackeray, J. T. 2007. Influence of electrode microstructure on the reactivity of Cu_2Sb with lithium, Electrochimica Acta,52(17): 5339–5345

[6] Rajgarhia, R. K.; Saxena, A.; Spearot, D.E.; Hartwig, K. T.; More, K. L.; Kenik, E.A and Meyer, H.2010, Microstructural stability of copper with antimony dopants at grain oundaries: Experiments and molecular dynamics simulations, J. of Materials Science, 45(24): 6707–6718.

[7] Fransson, L. M. L.; Vaughey, J. T.; Benedek, R.; Edström, K.; Thomas, J. O. and M. M. Thackeray. 2001. Phase transitions in lithiated Cu_2Sb anodes for lithium batteries: an in situ X-ray diffraction study, Electrochemistry Communications, 3(7): 317-323.

[8] Cooper, M. J. 1985. Compton scattering and electron momentum determination, Progress Physics, 48(4): 415-481 and references therein. Cooper, M. J., Mijnarends, P. E., Shiotani, N. Sakai, N. and Bansil, A. 2004, X-ray Compton Scattering(Oxford University Press , New York).

[9]Sharma, B. K.; Gopta, A.; Singh, H.; Perkki, S.; Kshirsagar, A. and Kanhere, D.G.1988, Compton profile of palladium, Phys, Rev, 37(12): 6821.

[10] Timms, D. N. 1989. Ph. D. Thesis University of Warwick, UK, unpublished.

[11] Felsteiner, J.; Pattison, P. and Cooper, M. J. 1974. Effect of Multiple Scattering on Experimental Compton Profiles: A Monte Carlo Calculation, Philosophical Magazine, 30(3):537-548.

[12]R. Dovesi, V. R.; Saunders, C.; Roetti, R.; Orlando, C. M.; Zicovich-Wilson, F.; Pascale, B.; Civalleri, K.; Doll, N. M.; Harrison, I. J.; Bush, P.; D'Arco and M. Llunell, CRYSTAL09. 2009. CRYSTAL09 User's Manual. University of Torino, Torino.

[13] Becke, A. D. 1993. Densityfunctional thermochemistry. III. The role of exact exchange, J. Chem. Phys, 98(7):5648-5652.

[14] Perdew, J. P.; Burke, K and Ernzerhof, M. 1996. Generalized Gradient Approximation Made Simple, Phys. Rev. Lett. 77(18):3865-3868.

[15] Kresse, G. and Joubert. 1999. From ultrasoft pseudopotentials to the projector augmented-wave method, J. Phys. Rev. B 59(3):1758.

[16] Biggs, F.; Mandelsohn, L.B and Mann, J. B. 1975. Hartree-fork compton profiles for the elements, Atom. Data Nucl. Data Tables, 16:201 -309

دراسة التركيب الالكتروني لمركبCu_2Sb باستخدام تقنية استطارة كومبتون

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الخلاصة:
في هذا البحث تم قياس كثافة الزخم الالكتروني عمليا لمركب(Cu_2Sb) باستخدام مطياف كومبتون ذي الطاقة ^{241}Am 59.54 keVوقدرة تحليلية (0.6 a.u.). قورنت القياسات العملية مع النتائج النظرية لمنحني كومبتون المحسوب بواسطة نظرية كثافة الدالية (DFT) ضمن الارتباط الخطي للمدارات الذرية (LCAO). اذ نلاحظ توافق نسبي بين النتائج النظرية ضمن (LCAO-DFT) والبيانات العملية المحسوبة لشكل منحني كومبتون. انجزت الحسابات للنموذج الايوني لعدد من الترتيبات $(Cu^{+x/2})_2(Sb^{-x})$ $(0.0\leq x\leq 2.0)$ ايضا باستعمال منحني الذرة الحرة .يفترض النموذج الايوني انتقال الكترونين من ذرة Cu ضمن المستوي 4s الى المستوي 5p لذرة Sb.

الكلمات المفتاحية: كثافة زخم الالكترون، قطع كومبتون، طريقة LCAO، الموديل الايوني، انتقال الشحنة.