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$_2$Sb 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$^-$) ($0.0 \leq x \leq 2.0$) 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$_2$Sb) crystallizes in a tetragonal system structure space group (P4/nmm), No 129 with two formula units per unit cell. The unit cell parameters are $a = 3.97$ Å and $c = 6.06$ Å, 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$_2$Sb and alloy powders as anode materials for lithium ion batteries. The nanoscale Cu$_2$Sb 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$_2$Sb as a promising anode material for lithium ion batteries. Sharma et al. [4] study the mechanism of lithium insertion/intercalation in the anode
In this paper, unless stated, all quantities are in atomic units (a.u.) where \( e=\hbar=m=1 \) and \( c=137.036 \), giving unit momentum=\(1.9929 \times 10^{-24} \text{ Kgms}^{-1} \), unit energy=27.212 eV and unit length=5.2918 \times 10^{-11} \text{ m}.

**Experimental:**

1- Synthesis of Cu$_2$Sb

Cu$_2$Sb 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 CuK$\alpha$ ($\lambda=1.5460\text{Å}$) source of X-rays, is shown in Fig.1

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°±3.0° by the sample of Cu$_2$Sb. The scattering chamber is evacuated to about 10$^{-2}$ Torr with a rotary oil pump 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 resolution n0.6 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 $\varphi_n(\mathbf{r,k})$ defined in terms of local function $\varphi_n(\mathbf{r})$ 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$_2$Sb 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$_2$Sb. 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 Cu2Sb. 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 (a.u.) | DFT-LCAO J(p) in e/a.u. | Ionic model | J(p) in e/a.u. | Experiment |
|---------|--------------------------|-------------|---------------|------------|
|         | (Cu^{+0.75})_{2}Sb^{2-} | (Cu^{+2})_{2}Sb^{2-} | (Cu^{+2})_{2}(Sb^{2-}) | (Cu^{+2})_{2}(Sb^{2-}) |
| 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      | 9.664      |
| 2       | 9.117                    | 8.849       | 8.878         | 8.910      | 8.944      | 8.712±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 ΔJ=J^{Theory}(p) - J^{Exp}(p) 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. range 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 χ² 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 Cu2Sb 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 1 a.u. All anisotropies are visible up to 2.0 a.u. Measurements on single crystalline samples of \( \text{Cu}_2\text{Sb} \) would be helpful to examine the directional features of bonding through anisotropies.

Conclusions:
Experimental Compton profile (CP) of polycrystalline \( \text{Cu}_2\text{Sb} \) 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 based Compton profiles. The difference \( \Delta J(p_z) = J_{\text{Theor}}(p_z) - J_{\text{Expt}}(p_z) \) 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.
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.

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دراسة التركيب الإلكتروني لمركب Cu$_2$Sb

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الخلاصة:
في هذا البحث تم قياس كثافة الزخم الإلكتروني عملية لمركب (Cu$_2$Sb) باستخدام طيف كومبتون ذي الطاقة 0.6 a.u. قدرة تحليلية 69.54 keV $^{241}$Am المحسوب بواسطة نظرية كثافة الدالة LCAO-DFT (LCAO-DFT) ونظريات الطاقة المحددة (LCAO) من مساحة الفضاء الوراثي لئة Cu في درجة Cu($^{4s}$) إلى Cu($^{4s}$) $^{5p}$ Sb

الكلمات المفتاحية: كثافة الزخم الإلكتروني، طريقة LCAO، الموديل الإلكتروني، انتقال الشحنة.