Nature of Bonding in Chromium Chalcogenides: A Compton Profile Study

L. VADKHIYA*, N. L. HEDA†, ALPA DASHORA* and B. L. AHUJA*

* Department of Physics, University College of Science,
M.L. Sukhadia University, Udaipur 313001, Rajasthan
Email: lvadkhiya@yahoo.com

We present the nature of bonding in chromium chalcogenides (CrX; X = S and Se) using equal-valence-electron-density (EVED) Compton profiles. For the Compton measurements, we have used 20 Ci 137Cs Compton spectrometer. We have also computed the Compton profiles using Hartree Fock (HF) and B3LYP schemes. The experimental EVED profiles suggest more localisation of charge in CrSe in comparison to CrS in the bonding direction. It is concluded that CrSe has more covalent character than that of CrS.

Key Words: Compton scattering, band structure calculation.

INTRODUCTION

Transition metal chalcogenides CrX (X=S, Se) have attracted much interest due to their technological importance, particularly related to their magnetic ordering due to combination of metal and chalcogen atoms. The binary CrX system crystallizes in the NiAs-type crystal structure. This structure consists of a hexagonal closed packing of metalloid atom with the transition metal atoms located in the interstices in such a way as to form a simple hexagonal array. These compounds show the phase transitions with the temperature and the hexagonal NiAs-type structure is stable at room temperature.

Regarding earlier important studies, the band structure calculations were performed for Cr-chalcogenides systems by Dijkstra *et al.*[1]. Koyama *et al.*[2] have studied the electronic structure of CrS with NiAs-type crystal structure using photoemission and inverse-photoemission spectroscopy.

It is well establish that the Compton scattering has become an important tool in investigating the electron momentum density in variety of materials.[3,4] In Compton scattering experiment, the aim is to obtain the Compton profile which is one- dimensional projection of the three-dimensional momentum density. In this paper, we present the nature of bonding in CrX (X = S and Se) using their Compton profiles.

---

† Department of Pure & Applied Physics, University of Kota, Kota-324005 (Raj.) India

EXPERIMENT

The electron momentum densities of CrS and CrSe were measured using our 20 Ci ^{137}Cs Compton spectrometer.[5] The incident beam of 661.65 keV γ-rays was scattered by the samples (in form of pellets) through a mean angle of 160 ± 0.6^{0}. The energy spectrum of the scattered photons was measured using a Ge detector (Canberra, USA) and the associated electronics like spectroscopy amplifier, analog to digital converter and multi-channel analyzer. An overall momentum resolution of the Compton spectrometer was 0.39 a.u. (Gaussian full width at half maximum).

Raw data for the CrS and CrSe were accumulated for a total period of 180 and 149 h, respectively. To extract the true Compton line shape, the raw Compton spectrum was corrected for several systematic corrections like background, instrumental resolution, sample absorption, detector efficiency, Compton cross-section and triple scattering in the sample.[6,7] The background contribution was measured under the identical conditions without keeping the sample in the sample holder. For the multiple (triple) scattering corrections, we have employed Monte Carlo simulations.[8]

THEORY

We have computed the electronic structure of CrS and CrSe using linear combination of atomic orbitals (LCAO) within the HF and hybridization of HF and Kohn-Sham (KS) approximation as facilitated in the CRYSTAL03 code[9-11]. In this code, the hybridization of HF and density functional theory (DFT) as suggested by Lee, Yang and Perr is known as B3LYP.

The all electron Gaussian basis sets for Cr, S and Se were taken from the www.tcm.phy.cam.ac.uk/_mdt26/basis_sets. To enhance the accuracy of basis sets, the energy optimization of the basis sets for CrS and CrSe was undertaken using BILLY program.[9,10] The lattice parameters for the NiAs-type structure of CrS (CrSe) were taken as a = b = 3.456 (3.674) and c = 5.761 (6.001) Å. While comparing with experiment, all the theoretical directional profiles were normalized to free atom Compton profile area.[11]

RESULTS AND DISCUSSION

Figs. 1 (a-b) show the difference between the theoretical and the experimental profiles of CrS and CrSe. To mimic the instrumental resolution, the isotropic theoretical profiles were convoluted with the experimental resolution function of 0.39 a.u. It can be seen that the present calculations exhibit almost similar type of differences with the experiment. For both the samples, particularly in the low momentum range say p_z < 3.0 a.u., we observe deviations between the theoretical profiles and the corresponding experiment. In the high

momentum region ($p_z > 4$ a.u.), a good agreement between the present measurements and the theoretical data confirms the correctness of data analysis procedure.
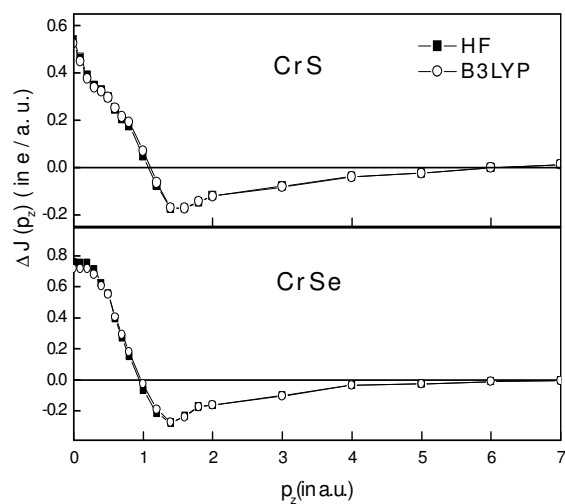

Fig. 1: Differences between the isotropic experimental and the convoluted theoretical profiles using HF and B3LYP schemes of CRYSTAL03 code
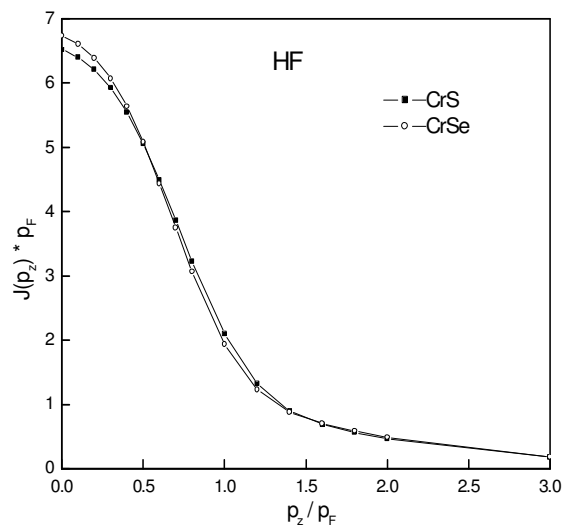

Fig. 2: EVED profiles (on p_z/p_F scale) of isoelectronic compounds CrS and CrSe for HF

To compare the relative nature of bonding in the isoelectronic CrS and CrSe, we have scaled our experimental and convoluted HF profiles to EVED. The EVED profiles are shown in Fig. 2. Both the EVED profiles were normalized to six valence electrons in the momentum range 0–6 a.u. The similarity in the EVED profiles may suggest that to first order the wave function for bonding electrons in both the isoelectronic materials may be identical. It is seen from Fig. 2 that near $p_z = 0$ a.u., both the theoretical and the experimental EVED profiles of CrSe are higher than that of CrS. Since the covalent bonding is a result of sharing of electrons, it increases localization of charge in the direction of bonding leading to a sharper Compton line shape. Therefore, our EVED profiles show that CrSe is more covalent than CrS.

ACKNOWLEDGEMENT

REFERENCES

1. J. Dijkstra, C. F. van Bruggen, C. Haas and R. A. de Groot, *J. Phys.: Condens. Matter,* **1,** 9163 (1989)
2. M. Koyama, H. Sato, Y. Ueda, C. Hirariand and M. Taniguchi, *Solid State Commun.*, **125**, 243 (2003)
3. M. J. Cooper, *Rep. Prog. Phys.,* **48**, 415 (1985) and references therein.
4. M. J. Cooper, P. E. Mijnarends, N. Shiotani, N. Sakai and A. Bansil, *X-ray Compton Scattering*. Oxford Science Publications, Oxford University Press, New York (2004) and references therein.
5. B.L. Ahuja, M. Sharma and S. Mathur, *Nucl. Instrum. Meths. B*, **244**, 419 (2006).
6. D. N. Timms, *Compton scattering studies of spin and momentum densities*. Ph.D. Thesis, University of Warwick, UK (unpublished) (1989).
7. J. Felsteiner, P. Pattison and M. J. Cooper, *Phil. Mag.,* **30**, 537 (1974)
8. C. Pisani and R. Dovesi, *Int. J. Quantum Chem.*, **17**, 501 (1980).
9. M. D. Towler, A. Zupan and M. Causa, *Comp. Phys. Commun.*, **98**, 181 (1996).
10. V. R. Saunders, R. Dovesi, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, N. M. Harrison, K. Doll, B. Civalleri, I. J. Bush, Ph. D'Arco and M. Llunell, *CRYSTAL03 User's Manual*, University of Torino, Torino (2003).
11. F. Biggs, L. B. Mendelsohn and J. B. Mann, *Atom. Data Nucl. Data Tables,* **16**, 201 (1975).