Cuprous halides: Old facts and new developments

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Cuprous halides are characterised by (a) large amplitude Cu$^+$ motion relative to immobile halide ion cage and (b) non-integral electron transfer from Cu to halogen. Recent theoretical work on Cu$^+$ ion dynamics in Cu-halides derived from two body interatomic potentials is reviewed in the perspective of experimental diffusion and conduction of CuBr & Cul. Calorimetric data on phase transitions in Cul have been analysed. Thermal expansion in strong anharmonic systems and its intimate connection to EXAFS has been pointed out.

1 Introduction

Cuprous halides, CuX ($X =$ Cl, Br, I) are solids with tetrahedral pseudo-ionic metal halogen bond and a stable halide framework that supports considerable cationic disorder even at moderate temperatures. CuCl transforms from zinc-blende to wurtzite at 681 K, which is stable up to the melting point (703 K). CuBr transforms from zinc-blende to wurtzite at 664 K and from wurtzite to superionic bcc structure at 744 K, which is stable up to the melting point (765 K). And Cul transforms from zinc-blende to a wurtzite-like phase at 642 K and back to a disordered fcc superionic phase at 680 K, which is stable up to the melting point (878 K). In the case of CuBr$^+$ and Cul$^+$, the temperature dependence of ionic conductivity (log $\sigma$ vs. $1/T$ plots) is highly nonlinear, symptomatic of the unusual ionic diffusion modes (Fig. 1). The ‘diffusion anomaly’ in Cu-halides namely the anomalously low diffusion observed in Cul relative to CuBr and CuCl has been discussed recently in terms of interionic potentials. Simple free-volume picture, however, predicts increasing diffusion from CuCl to Cul through CuBr, as the anion size increases from Cl-Br-I. Molecular Dynamics (MD) studies$^4$ of the ionic conduction mechanism in Cul concluded that the intermediate range interactions control the crystal structure through polarization terms in the two-body potential. These potentials control the diffusion constants and phonon density of states in Cu-halides. Highly correlated diffusional motion of ‘Cu$^+$-chains’ seems to occur in $\gamma$-Cul. Furthermore, the rms displacement of cations

![Fig. 1 — Log($\sigma$T) vs. 1000/T plots for CuBr (Ref. 1) and Cul (Ref. 2)](image)
follow a step-like behavior for potentials that produce low diffusion constants, in agreement with experiment in all the three phases, γ, β, and α-Cul. The direction of the largest anharmonic $\text{Cu}^+$ vibrations are towards the faces of tetrahedral cages, while the directions of diffusion are towards the edges of the cages. Significantly the local structure in γ-Cul changes in response to the motion of $\text{Cu}^+$ ions. The potential energy of the system which is a minimum at the tetrahedral site (for $\text{Cu}^+$) rises rapidly as the octahedral site is approached. Thus, as the temperature is increased, the deep energy minimum of octahedral site would become shallow so as to facilitate $\text{Cu}^+$ passage through such sites, resulting in an effective single particle $\text{Cu}^+$ motion in the α-phase. In a very interesting MD study on α-Cul, Ihata and Okazaki used the pair-wise potential with an effective charge of 0.70e (instead of 0.60e used by Vashishta & Rahman and 0.81e used by McGreevy et al.) to obtain $\text{Cu}^+$ diffusion coefficients in accord with tracer diffusion experiments. Also, by a polyhedron analysis, they examined the cation migration in α-Cul to find a 35 % octahedral site occupancy of $\text{Cu}^+$ in good agreement with EXAFS results. The most important conclusion emerging from these works is the realization of the need for including in the interatomic potential-many body contributions to cation-cation and cation-anion repulsion during diffusion. The 'effective charge' mentioned above actually means a "transverse charge" $Z_T$, which has been obtained from a rigorous quantum mechanical calculation (LCAO method) taking account of the localized d-electrons. Table 1 gives the $Z_T$ values and ionicities for the cuprous halides.

Aniya has attempted to understand the superionic conduction in general and Cu halides in particular from an electronic theoretical viewpoint. The real space pseudo-potentials are found to be strongly material dependent with the halogens determining the positive plateau of the potential. Most interestingly, the magnitude of the pseudo-potential in the region between 2d/8 and 6d/8, where d is the length of the body diagonal in the zinc-blende lattice, correlates with the appearance of superionic transport. From a fundamental physical point of view, the inter-atomic potential energy and the effective charge are influenced by the mutual interactions between the 3d-electronic and the ionic subsystem which decide the vibrational spectrum and the electronic band structure of these materials. Cuprous halides seem to satisfy very well the two criteria for superionic conduction: (1) vibrational amplitude of the mobile ion is greater than that of 'cage' ions and (2) chemical valence is non integral. To sum up, all these theoretical investigations, besides establishing a microscopic basis for Cu halides, stress that (pseudo)potential is the key to understanding the diffusion & conductivity in these (and related) materials.

Apart from the electrical properties that continue to be a challenge, cuprous halides show interesting excitonic spectra (Fig. 2). Recently, CuCl and CuBr quantum dots have been obtained and studied in the excitonic

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<th>Table 1 — ΔN and related parameters</th>
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<td>Ionicity $^a$</td>
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$^a$ Ref. 8b. Ref. 13

![Fig. 2 — Exciton Absorption in CuBr (Ref. 12) and Cul (Ref. 2) thin films at room temperature. Energy gap of Cul is found to be 3.204eV. The absorption bands labelled $Z_1, Z_2$ and $Z_3$ corresponds to the lower excitonic states. $H_1$ and $H_2$ are the doublets](image)
region from the point of view of luminescence, transient & persistent spectral hole burning application respectively\textsuperscript{11,12}.

In this article, we shall discuss three specific aspects of these compounds: (a) fractional electron transfer, (b) phase transition kinetics and (c) thermal expansion and extended X-ray absorption fine structure (EXAFS).

2 Fractional Electron Transfer

To start with, in CuX, treated as I-VII semiconductors, the Cu-X interactions dominate the band structure. The band gap is phenomenologically given by

\[ E_g(Cu-X) = \Delta(Cu-X) - \frac{1}{2} \Delta(X-X) - \frac{1}{2} \Delta E_g(Cu-Cu) \]  \hspace{1cm} \text{(1)}

where the second and third terms represents the van der Waals and valence shell repulsion energies respectively. The crucial point is that the Cu-X bond is not completely ionic and thus 'electron transfer' from Cu to X is not integral but fractional. One can develop a fractional electron transfer model\textsuperscript{13} to seek a connection between the nature of the superionic bond and parameters that determine electrical conductivity-namely mobile ion concentration, (effective) ion charge and ion mobility. The fractional electron transfer \( \Delta N \) as applied to CuX, is given by,

\[ \Delta N = \frac{(\chi_X - \chi_{Cu})}{2 (\eta_X + \eta_{Cu})} \]  \hspace{1cm} \text{(2)}

where \( \chi_X, \chi_{Cu} \) are electronegativities and \( \eta_X, \eta_{Cu} \) are chemical hardnesses of X and Cu respectively. In the density functional theory, \( \chi \) and \( \eta \) are defined as negative of chemical potential and derivative of total energy of the N-electron system (a superionic molecule) with respect to \( N \) at constant volume. Essentially, \( \Delta N = \Delta N_{covalent} + \Delta N_{ionic} \) and ranges from 0.54 (very ionic, CsF) to 0.04 (almost completely covalent, CsH\textsubscript{3}NH\textsubscript{3}). Table 1 lists the \( \Delta N \) values for Cu halides. This non-integral electron transfer together with statistical cation disorder could be the cause of the unusual electrical conductivity profiles of CuBr and CuI.

3 Phase Transition Kinetics

It would be interesting to investigate the nature of phase transitions by a thermal analytical tool such as the differential scanning calorimetry (DSC). Here, we shall present and discuss the results on Cul. Similar studies on CuCl and CuBr would give a complete picture of the origin of phase transition.

In DSC, enthalpy changes or changes of heat capacity produced by the physical processes, such as structural phase transitions in crystals and crystallization of glasses, are detected as endothermic and exothermic 'peaks' due to absorption or evolution of heat, as the sample is thermally scanned in the calorimeter. Fig. 3 shows the typical DSC thermogram for a commercial sample of Cul, heated at the rate of 10°C per minute.

Fig. 3 — (a) DSC of phase transitions in Cul. Note the hysteresis due to thermal cycling, (b) Kissinger plots [\( \log(\phi/T_m^{-2}) \) vs. \( 1/T \)] for \( \gamma-\beta \) and \( \beta-\alpha \) phase transitions in Cul.
The two endothermic peaks represent phase transitions of CuI from γ-β and from β-α phases respectively. Considerable thermal hysteresis is associated with these phase transitions when the sample is subjected to a heat-cool cycle, with transitions occurring at a lower temperature during the cooling cycle. Enthalpies of transition for both these transitions are calculated from the area (A) under the thermogram using the equation,

\[ \Delta H = kA/M \] ...

where \( M \) is the mass of the sample and \( k \) is the calibration constant. As the transition temperature and the height of the DSC peak are strongly heating rate dependent, one can consider these phase transitions as thermally activated kinetic processes and evaluate the activation barriers by analyzing the thermograms recorded for several heating rates on a given sample.

According to Kissinger\(^{14}\), one can determine the activation energy for a 'reaction' of any order from an analysis of the experimental variation in the peak temperatures with heating rates. In the case of CuI, both the phase transitions are regarded as 'reactions' so that the relation,

\[ \frac{d(\phi/T_n^2)}{d(1/T)} = \frac{E}{R} \]

... (4)

where \( E \) is the activation energy for the transition and \( R \) is the universal gas constant.

The heating rate \( \phi \) and the peak temperature \( T_m \) could be used to determine \( E \).

Fig. 3 shows the typical plot of \( \log(\phi/T_n^2) \) vs. \( 1/T \) for the 'heating' routine of γ-β phase transition in CuI. (Such plots have been obtained in the 'cooling' routine and also for the β-α phase transitions as given in Ref. 2). The slope of this plot gives the activation energy, the values of which are given in Table 2. Although we are dealing with the change from zinc-blende to wurtzite and wurtzite to bcc structures, we nevertheless regard them as 'reversible crystallization' of α-β phase from the β-phase, and of the β-α phase from the γ-phase and vice versa. This approach takes us to the model of Erukhimovitch and Baram\(^{15}\) for non-isothermal crystallization kinetics. In this model, the Kissinger procedure is applicable only when the nucleation of β- and α-phases proceeds by a heterogeneous mechanism with size saturation, which is valid in the present case where continuous (rather than pulsed) heating is employed. We suggest that a modulated DSC study would reinforce these inferences.

### 4 Thermal Expansion and EXAFS

Thermal expansion of solids is a very fundamental thermo-physical property that is connected not only with macroscopic volume changes and microscopic disorder but also with the basic interatomic forces operating in the solid. This is more true for cuprous halides, where the Cu\(^+\) disorder and the Cu-Br/I potential (which could be like \( V(r) = A r^{-8} - C/r \)) are both strongly temperature dependent and anharmonic. By way of an example, consider the linear expansion coefficient\(^{16}\) of Ag\(_{0.9}\)Cu\(_{0.1}\)Br relative to AgBr (Fig. 4). The dominant

![Fig. 4 — Thermal expansion of Ag\(_{0.9}\)Cu\(_{0.1}\)Br relative to AgBr (Ref. 16). Note the anomaly around 210°C.](image-url)
structural change brought in by just 10% CuBr is reflected in the defect-related anomaly around 210 °C which is absent in AgBr. Fig. 5 shows the temperature dependence of the Cu-Br distance studied by XRD and EXAFS. This curve shows the intimate connection between thermal expansion and EXAFS. In EXAFS, one measures the ‘fine structure’ (up to ~1000 eV) above the X-ray absorption edge (K or L shell) of a solid. This ‘fine structure’ is oscillatory in nature and is due to local structure-dependent interference effects. This ‘interference’ in fact leads to a modulation of X-ray absorption coefficient by neighboring atoms. Thus one gets-after extensive analysis using theoretical models-information about the environment of the absorbing atom (Cu^+ in the present case). EXAFS actually measures an average of the electron transition probability over instantaneous distances. Yang and Joo^{17} analysed the EXAFS of the anharmonic vibrational systems by connecting the asymmetric pair distribution parameter (δ) to the local thermal expansion. Further, this parameter is related to the second and ‘third cumulants’ in the cumulant expansion of the potential,

\[ V(r) = -K_B T \sum_{n=0} C_n (r - r_0)^n \]  

where

\[ C_n = (-1)^{n-1} \frac{s}{n(s+1)^2} \delta^n, \text{ for } n \geq 2 \]  

where s is the weighting factor, r₀ is the equilibrium distance about which the expansion is measured and δ the skewness of the distribution which relates to the local thermal expansion, is given by the useful relation

\[ \delta = \frac{C_3}{2C_2} \]  

Fig. 5 — Temperature dependence of Cu-Br distances from XRD and EXAFS (Ref. 18)

which enables correlation of the two experimental quantities α and δ. A recent EXAFS study on CuBr^{18} carried out over a temperature range 300 - 631 K has established that (i) a potential minimum position for the nearest neighbour pairs of Cu and Br decreases monotonically and (ii) the mean interatomic distance totally expands due to anharmonic vibrations, upon increasing temperature. Anharmonicity of lattice vibrations, which gives rise to structural instability and thermal expansion anomalies as in CuI (Fig. 6) also deforms from the EXAFS spectrum significantly. The anomaly observed at the γ-β phase transition which is in accord with the volume changes observed in X-ray and Neutron diffraction^{19} is accountable in terms of negative pressure developing in the system.

5 Conclusions

Cuprous halides - especially CuBr and CuI - are characterized by tetrahedral Cu-Br/I bonding, non-linear conductivity due to high correlated Cu^+ -ion motion. Incomplete electron transfer and non-integral effective charge and anharmonicity arise from mutual interactions between 3d-electronic & ionic subsystems. Phase transitions in CuI from zinc-blende to wurtzite and from...
wurtzite to fcc phase are characterized by DSC peak analysis as 'crystallization reactions' in terms of Kissinger plots justified by Erukhimovich-Baram model. Thermal expansion of CuI shows a large anomaly at γ-β transition, accountable by the development of negative pressure. EXAFS is shown to have an intimate connection with thermal expansion.

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