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Study of copper ion superionic solids in the system $(1 - x)\mathrm{CuI}:x\mathrm{CdI}_2$

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Electrical transport studies of five compounds ($x = 0, 0.25, 0.33, 0.50$ and 0.75) in the system $(1 - x)\mathrm{CuI}:x\mathrm{CdI}_2$ have been reported. It has been observed that all compounds of this system undergo phase transition from lower temperature low conducting β-phase to higher temperature high conductivity α-phase. The phase transition temperature (T_p) decreases systematically with x being 642 for $x = 0$ and 500 K for $x = 0.50$. Above T_p all compounds are typical superionic solids with Cu^+ ion as the entity of charge carrier. From the stability, temperature span of superionic phase, T_p and σ values point of view $\mathrm{Cu}_3\mathrm{CdI}_5$ ($x = 0.25$) appears to be the best superionic solid of this system. The extended lattice gas model has been shown to suit better for explaining the electrical transport of solids with $0 \leqslant x \leqslant 0.5$ of this system in superionic solid phase. Below T_p all compound of this sytem behave as normal ionic solid with relatively high conductivity. They yield usual "Knee temperature" and below this temperature conductivity becomes extrinsic. The activation enthalpy, heat of transport and enthalpy for the formation of defects have also been evaluated from experimental electrical conductivity and thermoelectric power data in each case.

1. Introduction

Considerable interest has been witnessed towards development, study and application of solid electrolytes popularly known as solid superionic conductors (SSIC) in recent years. Useful solid electrolytes which have been developed during the last sixteen years are mostly silver ion conductors [1–7]. Since copper is cheaper compared to silver, it is more meaningful to search copper based SSIC for practical applications. Various attempts have been done [8–17] in this direction during the last few years and many good copper ion SSIC have been reported. It appears that thorough investigation of electrical transport properties of mixed copper salts is needed to get better copper ion SSIC. This paper is an attempt in this direction and reports the electrical transport study of some compound in the system $(1 - x)\mathrm{CuI}:x\mathrm{CdI}_2$.

2. Material preparation and experimental techniques

CuI and CdI_2 powders, with stated purity of 99.99% procured from M/S Bonds, New Delhi, India, were used as such in the preparation of these compounds. They were mixed in stoichiometric proportion, pelletized and heated in sealed pyrex tube around 500 K for ten hours. It was reground, pelletized, sealed in the pyrex tube and then melted and cooled to room temperature. Compounds prepared with different values of x have well defined melting points which decrease systematically with increase of x. The prepared compounds were ground in form of fine powders, using agate mortar and fine grid structure which were then used for further studies. For measurement of electrical conductivity (σ) and thermoelectric power (S) fine grained powders of these compounds were pressed in form of pellets of about $10^{-4}\,\mathrm{m}^2$ area and 1×10^{-3} to $5 \times 10^{-3}\,\mathrm{m}$ in thickness at a pressure ranging from 2×10^7 to $10 \times 10^7\,\mathrm{kg\,m}^{-2}$. The pellet faces were made smooth and flat by grinding and were cleaned by benzene. Flat thin metal foils were mechanically pressed or conducting paint gently painted and dried on two faces of the pellet to serve as electrodes. Usually pellets with electrode on were

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heated up to nearly the melting point of the compound before taking measurement on σ and S. The σ and S measurement were done using the procedure as described elsewhere [17, 18].

3. Result and discussions

Five compounds namely ($x = 0$, 0.25, 0.33, 0.50 and 0.75) of the system $(1-x)\text{CuI}{:}x\text{CdI}_2$ have been prepared and studied. First σ, S and density (d) of few pellets of each compound made at different pelletizing pressure (P) have been measured at few constant temperatures. Slightly larger value of σ is always obtained for higher P pellet in case of each compound. However, a graphical plot shows that increase of σ up to P value of about $4 \times 10^7 \text{kg m}^{-2}$ is faster but for $P > 6 \times 10^7 \text{kg m}^{-2}$ a trend of constancy is observed in σ values and practically they become independent of P. The relatively low conductivity observed for pellets prepared at low pressure is likely to be due to presence of low conducting air space and grain boundaries. Obviously these are considerably reduced at higher P values. This is further evidenced from the measurement of density. In case of each material it also becomes independent of P when the latter exceeds 6×10^7 kg m^{-2}. S values in the case of each compound are observed to be nearly constant for pellets made at higher P, however, slightly larger values of S are obtained for pellets made at lower P. Further σ has been measured as a function of a.c. signal frequencies $f = 0 \sim 10^4$ Hz. The values have been found independent of f indicating that in pressed pellets grain boundary effects are insignificant. Both σ and S values have been found independent of the dimension of the pellet. All above observations indicate that measurement of d, σ and S done on pellet made at $P > 6 \times 10^{-7} \text{kg m}^{-2}$ represents the bulk value of the material and are nearly free from air space and grain boundary effects. Both σ and S do not depend much on electrode material, however, maximum value of σ and minimum value of S are obtained using copper foil electrodes mechanically pressed on the faces of the pellet and measurement done after heating the pellet to slightly higher temperature.

The electrical conductivity (σ) of several pellets of each compound made at $P > 6 \times 10^7 \text{kg m}^{-2}$ has been measured at different temperatures using copper foil electrode. The mean σ values of the first cooling cycle of some compounds ($x = 0$, 0.25, 0.33, 0.50 and $x = 0.75$) are shown in Fig. 1 as log σT against T^{-1} plot. It is seen from this figure that these curves are linear from highest temperature reached to a temperature (T_3). Just below T_3 curves (not very clear for $x = 0.75$) show a steep minima. Few degrees below this minima (say from T_2) the curve again shows linear decrease with T^{-1}. However, a change in the slope of this linear variation occurs around temperature T_1 but plots remain linear down to room temperature.

It is well known [10, 15] that CuI goes into phase transformation around 642 K. We observed that this temperature is equal to the mean of T_3 and T_2 and lies very close to the temperature at which minima is observed in electrical conductivity log (σT) against T^{-1} plot. These plots for other solids of this system are similar to that of CuI. Thus minima in the σ variation of these solids, like in CuI, indicates a structural phase transition from β to α-phase. The phase transition temperature (T_P) may be taken as the temperature at which minima occurs in log (σT) against T^{-1} plots. The evaluated values of T_P for all solids are given in Table I along with the values of T_1, T_2 and T_3.

Like σ, S of few pellets made at $P > 6 \times 10^7$ kg m^{-2} of each compound has been measured as a function of temperature. The S against T^{-1} plots for some solids of this system which have σ values larger than $1\,\Omega^{-1}\text{m}^{-1}$ at T_3 are shown in Fig. 2. It is seen from this figure that jump in S values occur at specific temperatures T'_3, T'_2, and T'_1. A typical S against T^{-1} plot is linear in the temperature ranges $T > T'_3$, $T'_2 < T < T'_1$ and $T < T'_1$. The phase transition temperature (T'_P) may be taken as taken as mean of T'_3 and T'_2. The values of T'_3, T'_P, T'_2 and T'_1 are given in Table II. It is seen that T'_3 and T'_P are only slightly different than T_3 and T_P. This difference in the break and phase transition temperatures observed from log (σT) against T^{-1} and S against T^{-1} plots may be due to the differeent conditions at which

TABLE I T_3, T_P, T_2 and T_1 for different compounds of the system $(1 - x)\text{CuI}{:}x\text{CdI}_2$

Compounds x values	T_3K)	T_P(K)	T_2(K)	T_1(K)
0.0	660	642	624	520
0.25	530	515	500	470
0.35	510	505	500	470
0.50	505	500	495	462
0.75	488	488	488	480

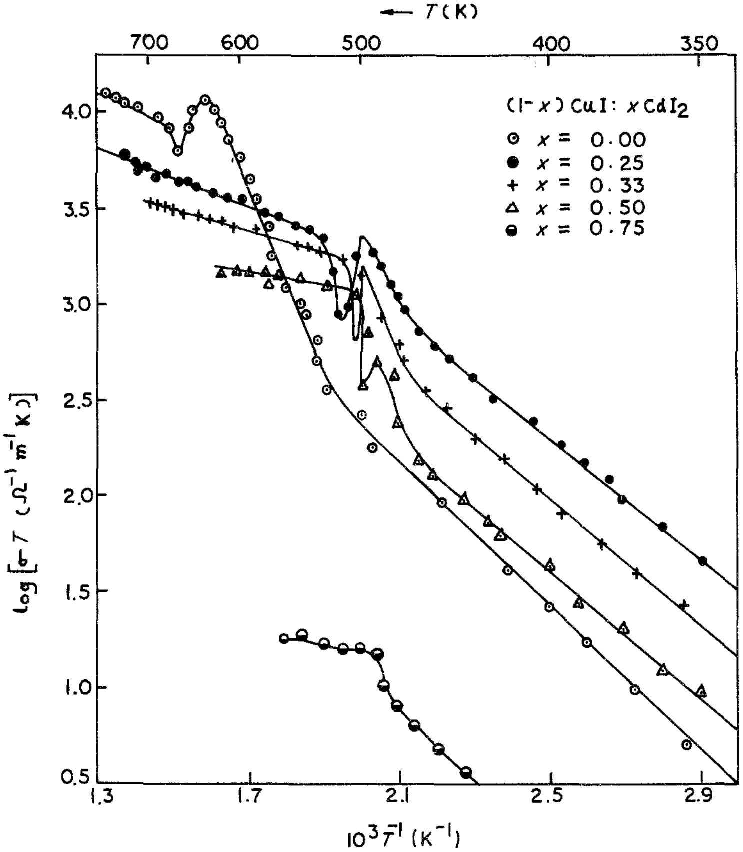

Figure 1 Plots of logarithm of product of electrical conductivity and temperature (σT) as a function of inverse temperature (T^{-1}) for the compounds in the sytem $(1-x)$ CuI:xCdI$_2$.

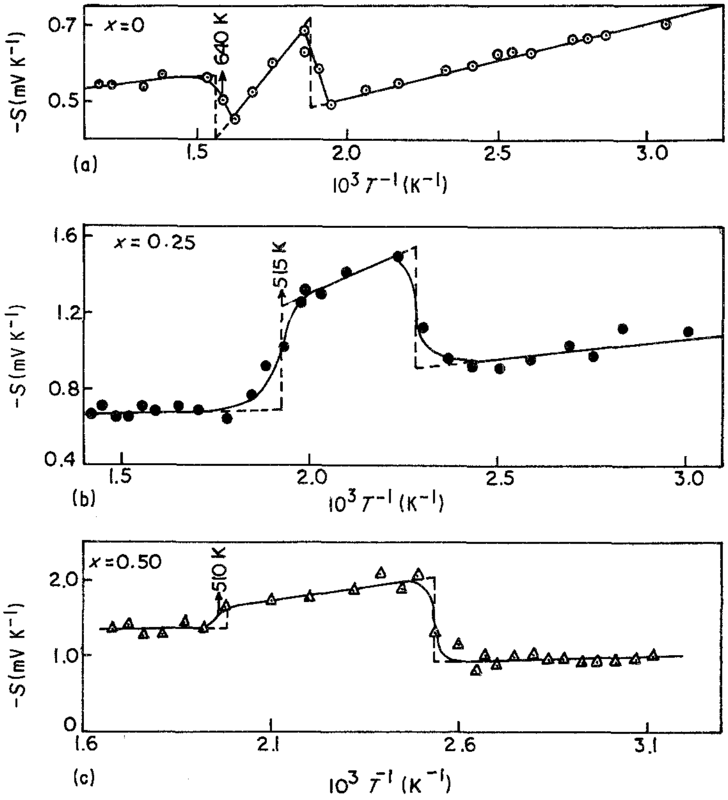

Figure 2 Plots of thermoelectric power (S) against inverse of absolute temperature (T^{-1}) for $x=0$, $x=0.25$ and $x=0.50$ compounds in the system $(1-x)$XuI:xCdI$_2$.

TABLE II Temperatures T_3', T_P', T_2' and T_1' as obtained from S against T^{-1} plot for the system $(1-x)$CuI:xCdI$_2$

x	T_3'(K)	T_P'(K)	T_2'(K)	T_1'(K)
0.0	650	640	630	525
0.25	530	515	500	440
0.50	515	510	505	395

sample is kept in both these measurements. In σ, measurement whole sample is kept at same temperature whereas in S measurement sample is subjected to thermal gradient and hence mean temperature in this measurement does not reflect the actual thermal state of the whole sample. Obviously, if something is happening in the sample it will be clearly reflected at the same temperature in σ but may be observed few degrees below or above in S measurement. Thus break and phase transition temperature appearing in log (σT) against T^{-1} and S against T^{-1} plots indicate the same happening in the sample.

On the basis of above data, it is convenient to examine the electrical conduction in these solids in three temperature ranges namely (i) $T > T_3$ (ii) $T_2 > T > T_1$ and (iii) $T < T_1$. The first temperature range corresponds to superionic or α-phase and the second and third for intrinsic and extrinsic ranges in normal ionic or β-phase of the solid.

(i) Electrical conduction in α or superionic solid phase – CuI in α-phase has structure similar to that of α-AgI and is a typical solid superionic conductor which for the sake of similarity of nomenclature will be referred as superionic solid (SIS) phase. Although we have not investigated the structure of compounds of CuI–CdI$_2$ system, yet the similarity of σ data of these solids with that of CuI infers that these compound undergo a phase transition into a cationically disordered solid, which are similar to α-phase of CuI. Therefore, all the compounds (e.g. $x = 0$, $x = 0.25$, $x = 0.33$ and $x = 0.50$) of this system which have σ values at T_3 larger than $1\,\Omega^{-1}\,\mathrm{m}^{-1}$ may be referred as solid superionic conductor.

A plot of σ values at T_3 (just above T_P) with x is shown in Fig. 3. It is seen from this figure that σ values decreases rapidly with x and becomes less than $1\,\Omega^{-1}\,\mathrm{m}^{-1}$ for compounds with $x > 0.50$. It has highest value for CuI. Thus from σ value point of view CuI is the still the best. All these compounds remain superionic conductor up to their melting point. Therefore, one can calculate the temperature span ($\Delta T = T_m - T_3$) over which these solids are in SIS phase. ΔT together with T_P has also been plotted as a function of x in Fig. 4. It is seen that ΔT is largest for Cu$_3$CdI$_5$ $(x = 0.25)$, and decreases for $x > 0.25$ and $x < 0.25$. T_P for compound $x = 0.25$ is much smaller than CuI and is not very much higher than T_P for other solids. Further compound with $x = 0.25$ has better stability than CuI in air at higher temperature. Thus for stability, span of SIS phase, phase transition temperature and also from σ values point of view Cu$_3$CuI$_5$ seems to be best SSIC in this system.

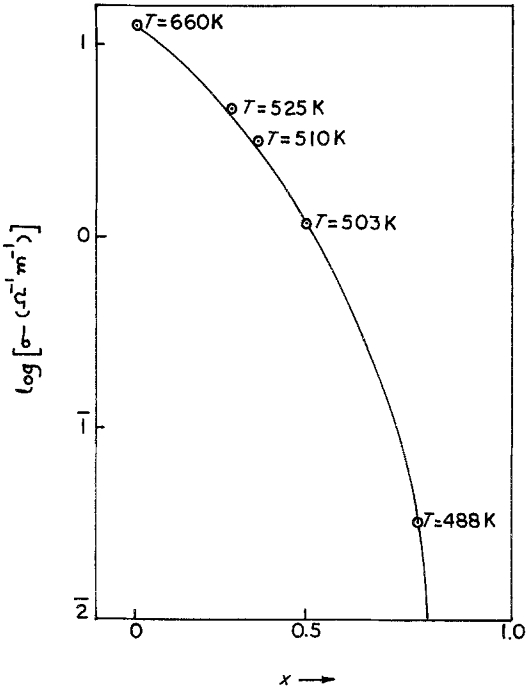

Figure 3 Logarithm of the electrical conductivity (log σ) at T_3 as a function of x in the system $(1-x)$CuI:xCdI$_2$.

It has been found that d.c. conductivity of Cu/$(1-x)$. CuI:xCdI$_2$/C (graphite) system for $T > T_3$ decreases with time and drops by about four decades in two hours. This indicate that for $T > T_3$, these solids are predominantly ionic conductor and electronic conductivity in them is less than $10^{-4}\,\Omega^{-1}\,\mathrm{m}^{-1}$. An extended form of S against T^{-1} plot for compound with $x = 0$, $x = 0.25$ and $x = 0.50$ for $T > T_3$ is shown in Fig. 5. It is seen from this figure that S values are negative over entire temperature range. Thus as per convention [19] positive ions should be the entities of charge carrier in these solids. Among the two positive ions namely Cu$^+$ and Cd^{2+}, the latter has a bigger size and contains a larger charge.

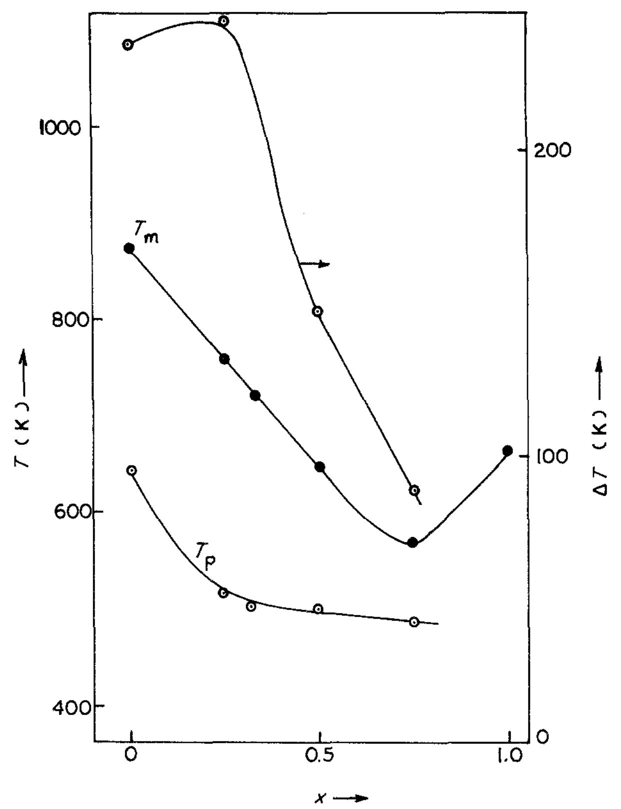

Figure 4 Melting point (T_m), phase transition temperature (T_p) and span of SIS phase (ΔT) as a function of x for the system $(1-x)$CuI: xCdI$_2$.

Thus from space availability and the coulomb repulsion point of view Cu^+ ion movement should be preferred over Cd^{2+} ion movement. The lowest value of S observed for copper foil electrode also speaks in favour of Cu^+ ion conduction. Thus we conclude that all compounds of $(1-x)CuI:xCdI_2$ system with $x > 0.5$ are superionic solid with Cu^+ ion as the main entity of charge carrier. The general expression for σ and S for such solids is given by the expression [5]

$$\sigma T = \sigma_c \exp(-h_m/kT) \quad (1)$$

and

$$S = -Q/eT + H \quad (2)$$

where σ_c is a constant, h_m is the activation enthalpy for the migration of Cu^+ ions, Q is heat

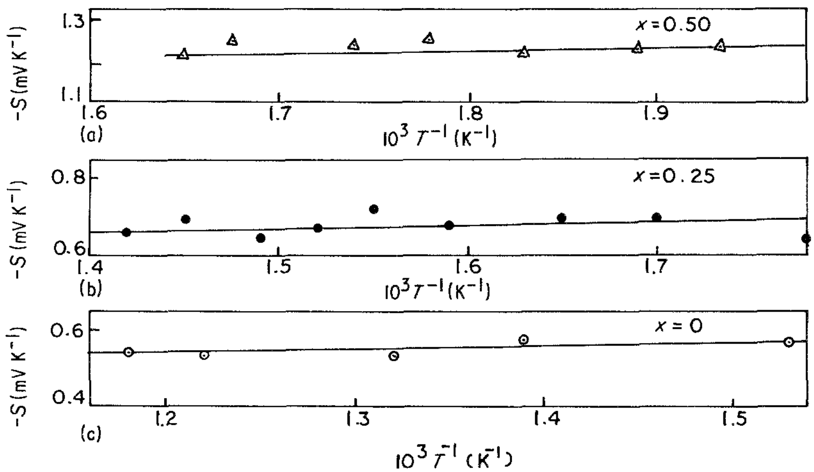

Figure 5 Plots of thermoelectric power (S) against inverse of absolute temperature (T^{-1}) for compounds with $x =$ 0, 0.25 and 0.50 in the superionic solid phase.

TABLE III Values of σ_c, h, Q and H for different compounds in the system $(1-x)$CuI:xCdI$_2$ in SIS phase

x	$\sigma_c(\Omega^{-1}\ \mathrm{m}^{-1}\ \mathrm{K})$	h_m (eV)	Q (eV)	$-H$ (mVK^{-1})
0.0	1.65×10^5	0.17	0.096	0.42
0.25	6.42×10^4	0.15	0.078	0.55
0.33	2.65×10^4	0.12	–	–
0.50	6.23×10^3	0.07	0.066	1.12

of transport for Cu$^+$ ion and H is a factor which depends upon several parameters but remain practically constant for such solids over larger temperature range. Thus plot of log (σT) and $\dot{S}$ with T^{-1} should be straight line for these solids. This has been found experimentally true for all solids as seen from Figs. 1 and 5. Evaluated values of σ_c, h_m, Q and H from these linear plots for different solids are given in Table IV.

Different models have been proposed in the literature to explain electrical transport mechanism in superionic solids. Important among these are free ion [20], lattice gas [21], ionic polaron [22], and extended lattice gas [23] models. Both free ion and lattice gas models predict the same value for h_m and Q. For solids of this system none of these have been found equal (Table III) and hence these two models are not appropriate for these solids. The extended lattice gas model predicts the following relation between h_m and Q.

$$2h_m = 2Q + E_B \tag{3}$$

where E_B is a quantity usually referred as ionic polaron binding energy and is given by the expression [22]

$$E_B = \frac{Z^2e^2}{2\pi^2\epsilon_0 a}\left(\frac{1}{K_\infty}-\frac{1}{K_0}\right) \tag{4}$$

where Ze is the charge on the mobile ion, ϵ_0 is the dielectric constant of the vacuum, a is the jump distance and K_0 and K_∞ are the static and optical dielectric constants of the solid in SIS phase. Since E_B is a positive quantity, hence h_m should be greater than Q. For compounds with $x = 0$ and $x = 0.25$ (Table III) h_m has been found greater than Q by 0.074 and 0.072 eV, respectively. Thus lattice gas model probably explains the situation in these solids. The exact evaluation of E_B is difficult because neither structure nor K_∞ and K_0 are available for these solids at present. This makes quantitative comparison of experimental and theoretical values of $(h_m - Q)$ difficult. However, an estimate of E_B can be made. For copper iodide our measurement* of K_0 gives its value of the order 10^2, K_∞ is about 10 and $a = 5.96\times10^{-10}$ m. This yields $E_B \simeq 0.138$ eV. This predicts difference between h_m and Q to be about 0.069 eV which is nearly same as obtained by us experimentally.

In case of compound with $x = 0.50$ we found that $h_m = Q$ and probably extended lattice gas model is not a suitable model for this. The ionic polaron model predicts $h_m = E_B$. However, no expression is available for S in this model. E_B, in the case of compounds with $x = 0.50$, will be nearly of the same order (10^{-1} eV) as for CuI. This is the order of h_m for $x = 0.50$. Thus ionic polaron model may describe the conduction in solids with $x > 0.50$, of this system in the conducting phase. This also indicates that structural arrange for a solid with $x = 0$ and $x = 0.25$ in α-phase is different than those of $x = 0.50$ and $x = 0.75$.

(ii) Electrical conduction in β or normal ionic solid phase: All compounds of $(1-x)$CuI:xCdI$_2$ system undergo a phase transition at T_p and below this temperature they exist in a phase which as per convention may be termed as β or normal ionic solid phase. The d.c. electrical conductivity of some of these compounds using

TABLE IV Pre-exponential factors (C and C'), apparent activation energies (E_a) and energy of formation for defect pairs (H_f) for solids of $(1-x)$CuI:xCdI$_2$ system

x	*High* temperature region $T_1 < T < T_2$		Low temperature region $T < T_1$		
	C $(\Omega^{-1}\ \mathrm{m}^{-1}\ \mathrm{K})$	$E_a = (H_f/2 + h_f)$ (eV)	C' $(\Omega^{-1}\ \mathrm{m}^{-1}\ \mathrm{K})$	$E_a - h_f$ (eV)	H_f (eV)
0.00	6.80×10^{11}	0.96	1.20×10^6	0.37	1.18
0.25	7.09×10^{11}	0.84	1.63×10^6	0.31	1.06
0.33	2.85×10^{12}	0.92	1.38×10^6	0.33	1.18
0.50	1.88×10^{12}	0.93	6.15×10^5	0.33	1.20
0.75	–	–	6.21×10^5	0.37	–

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*Because of very high loss, evaluation of K_0 becomes difficult at low frequencies.

copper electrodes on one side and graphite along the other side has been measured at fixed temperature lying below T_p as a function of time. σ decrease with time and becomes 100 times lesser than the initial conductivity. Graphite is the electrode which blocks ionic conduction. Thus all these solids in NIS phase are still predominantly ionic conductor. In such solids electrical conduction results due to (Schottky or Frenkel) defects. If both defects corresponding to cation and anion are mobile, then complete transport parameters can be obtained following either the procedure of Fuller *et al.* [24] or that of Chandra and Rolfe [25]. The S against T^{-1} plot for studied compounds is given in Fig. 2. S is large and has a negative sign, which indicates that positive mobile defects are the main entity of charge carrier. Of the two positive ions, namely Cu^+ and Cd^{2+}, the former will be preferred for conduction from volume availability and coulomb repulsion consideration. Frenkel defects are usually more mobile and hence we shall try to explain these results on the mobility of Cu^+ ion in interstitial position. The expression for conductivity in such a case is given by the expression [26]

$$\sigma T = C \exp(-H_f/2kT) \exp(-h_f/kT) \quad (5)$$

where C is a constant, H_f is enthalpy for the formation of defects and h_f is activation enthalpy for the migration of defects. Therefore, plot of log (σT) against T^{-1} will be linear with a slope corresponding to apparent activation energy (E_a)

$$E_a = H_f/2 + h_f. \quad (6)$$

The above expression holds good only in an ideal perfect sample or at high temperature in an otherwise imperfect sample. Normally at lower temperature, the exp $(-H_f/2kT)$ term is small and may be taken as a constant over a fairly wide temperature range [26]. Therefore, the variation of σ reduces to

$$\sigma T = C' \exp(-h_f/kT) \quad (7)$$

where $C' = C \exp(-H_f/2kT)$ is constant. This gives an apparent activation energy equal to h_f. Therefore, in practice for a normally pure sample the log (σT) against T^{-1} plots usually display two distinct linear regions, one at higher temperature (normally referred as the intrinsic region) which is associated with a higher slope $E_a = H_f/2 + h_f$ and at the lower temperature an extrinsic region which not only displays a lower slope $E_a = h_f$ but the magnitude of σ as well as E_a depends strongly on the purity and to some extent on the thermal history of the particular specimen employed. The temperature separating these two regions is referred as the "knee" temperature.

The log (σT) against T^{-1} curve Fig. 1 for all solids are linear below T_p in two distinct regions $T_2 > T > T_1$ and $T < T_1$ with former having higher slope as expected from theory. The values of C, $H_f/2 + h_f$, C' and h_f have been evaluated from these linear plots and are given in Table IV. The evaluated values of H_f for different solids are also listed in this table.

For ionic solids displaying Frenkel disorder, in contact with cation metal (e.g. Cu/CuI/Cu) the total thermoelectric power is given by the expreesion [6, 16]

$$S = S_{\text{hom}} = -Q/eT + H \quad (8)$$

where

$$H = 1/e\,[k \log(n/N) + \partial g/\partial T + S_1] \quad (9)$$

where Q is the heat of transport for the ion, n and N are number of defects and normal site per unit volume, g is the amount of work required to bring the cation (Cu^+ ion in our case) from a state of rest at infinity to an interstial position in the solid at constant temperature and pressure, and S_1 is the partial entropy of the Cu^+ ion in copper metal. The number n at any temperature can be expressed by the relation

$$n = (NN')^{1/2} \exp(-H_f/2kT) \quad (10)$$

where N' is the number of interstial site per unit volume available to Cu^+ ion. Since both N and N' are of the same order, one can write from the above equation

$$k/e \log(n/N) = -(H_f/2eT). \quad (11)$$

Using Equations 9 and 11 and noting that second and third term of Equation 9 are temperature dependent, although the increase of one nearly compensates the decrease of the second and thus their sum can be approximately taken as equal to a temperature independent small constant S_2, we can write the expression for S (Equation 8) as

$$\begin{aligned} S &= -1/eT[Q + H_f/2] + S_2 \quad (12) \\ &= -Q_a/eT + S_2. \quad (13) \end{aligned}$$

This expression obviously refers to the intrinsic

TABLE V Apparent heat of transport (Q_a), S_1, H and H_f for some solids in the system $(1-x)$CuI:xCdI$_2$

x	Higher temperature region $T_2 > T > T_1$		Lower temperature region $T < T_1$		
	$Q_a = (H_f/2 + Q)$ (eV)	$-S_1$ (mV K^{-1})	$Q_a = Q$ (eV)	$-H$ (mV K^{-1})	H_f (eV)
0.00	0.85	0.89	0.20	0.11	1.30
0.25	0.84	0.30	0.20	0.46	1.28
0.50	0.80	0.00	0.17	0.43	1.26

region. For the extrinsic region where n can be taken approximately constant over the entire region, the expression for S remains same as given by Equation 9. However, H in this situation becomes almost independent of T. Thus a plot of S against T^{-1} in the NIS phase of these solids should also be linear with a jump in the S value and change in the slope at the knee temperature. The higher temperature region slope should yield $(Q + H_f/2)$ and lower temperature slope the value of Q. From these two one can find values of Q and H_f separately. The plots of S against T^{-1} (Fig. 2) for all studied solids are in accordance with the above conclusions. The evaluated values of Q_a, S_2, Q, H and H_f for different solids are given in Table V. From Tables IV and V we find that evaluated values of H_f from σ and S data are nearly the same. This further justifies that Cu$^+$ ions are the main entity of charge carrier in these solids.

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