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Influence of cadmium doping on the ionic conductivity and on the γ–β phase transition of copper(I) bromide[†]

Julio C. Bazan,[*][‡] **R. Susana Pettigrosso and Carlos O. Soria**

Departamento de Química e Ing.Química, Universidad Nacional del Sur, 8000 Bahía Blanca, Argentina

It was found that the addition of cadmium bromide to copper(I) bromide has a promoting effect on the γ-phase conductivity, together with a noticeable decrease of the γ–β transition temperature. A knee in the low temperature range of the Arrhenius plots of conductivity is interpreted as corresponding to the solubility temperature of $CdBr_2$ in CuBr.

One of the main goals in solid state electrochemistry is to improve the conductive properties of solid electrolytes. To this purpose, the so-called 'homogeneous doping' *i.e.* the replacement in the lattice of normal ions for homo or aliovalent foreign ions is a common procedure. In our laboratory, we have already studied the effect of introducing the homovalent Cs ion into CuI[1], AgI[1,2] as well as in CuBr,[3] in all cases having found an improvement of the conductive characteristics which was adscribed to a mechanical effect of 'lattice loosening' which induced a decrease in the energy of formation of the prevailing defects. In the present work, bivalent Cd^{II} was used as dopant for CuBr. Copper(I) bromide is a good ionic conductor, with a very low partial electronic conductivity. It exists in one of three different solid phases with transition temperatures of *ca.* 658 K (γ–β) and *ca.* 743 K (β–α).[4] The prevailing defects are of the Frenkel type. As the introduction of bivalent cadmium ions in place of monovalent copper(I) ions produces a cation vacancy for each cadmium ion, a consequent increase in conductivity was found. Besides, a decrease of the γ–β transition temperature was also observed, and the solubility curve of cadmium bromide in copper(I) bromide was obtained.

Experimental

Samples of CuBr containing 0, 0.39, 0.68, 1.03, 1.53, 2.00, 2.36, 3.29, 4.47, 5.00 and 7 mol% $CdBr_2$ were prepared by melting together the weighed amounts under pure nitrogen. The chemicals used were from Cerac Micropure and were of 99.99% purity. The dopant concentrations were checked by means of atomic absorption spectroscopy. The resulting mixture was ground and pressed into pellets of 7 mm in diameter and thickness of *ca.* 3 mm. The conductivity cell was assembled by pressing the pellets between high purity copper disks by means of stainless steel springs. The resistance measurements were carried out by means of either an Impedancemeter IM5d from Zahner-elektrik or a Wheatstone Bridge at fixed frequency of 1 kHz. The cell was placed in a glass furnace with temperature control to ±2 K and maintained under purified nitrogen. The temperature range examined was in the range 460–740 K, and the measurements were made both in heating and cooling cycles.

Results and Discussion

Fig. 1 shows Arrhenius-type plots of conductivity data for different mole percentages of cadmium bromide. The data pertaining to samples of pure CuBr are also plotted for comparison. In the high temperature region, down to the β–γ transition, the curves show no significant influence of the dopant. Thereafter, however, three important features appear: (1) a noticeable decrease in the γ–β transition temperature, (2) the expected conductivity increase, together with a decrease of the apparent activation energy for the γ phase and (3) a not dramatic but noticeable 'knee' at lower temperatures, *i.e.* a point after which the conductivity decreases with a consequent increase in the slope of the Arrhenius curve. All three effects are more pronounced at higher dopant concentration. At 7 mol% the temperature of the knee practically is the same as the temperature of the γ–β transition.

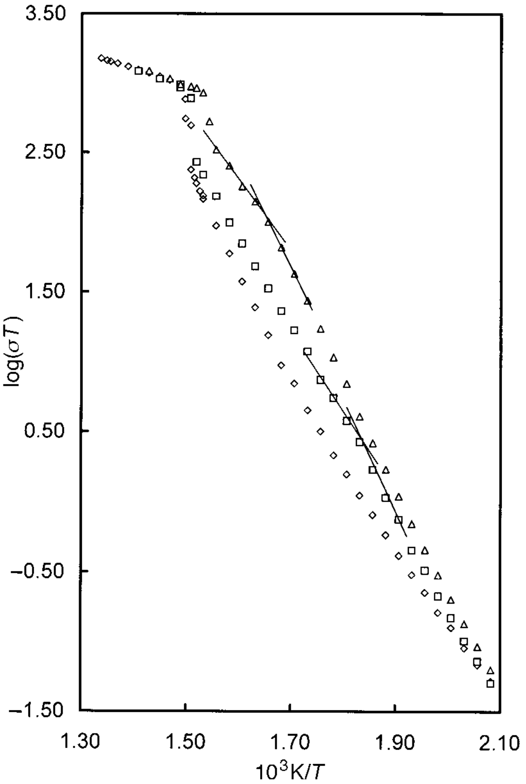

Fig. 1 Conductivity Arrhenius plots: ◇ pure CuBr; □ 0.68 mol% $CdBr_2$; △ 3.3 mol% $CdBr_2$. The intersection of the solid lines marks the 'knee' position.

Determinations made using the Wagner–Hebb method showed no apreciable effect of doping on the electronic conductivity.

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[‡] Research Fellow, CIC Province of Buenos Aires, Argentina.

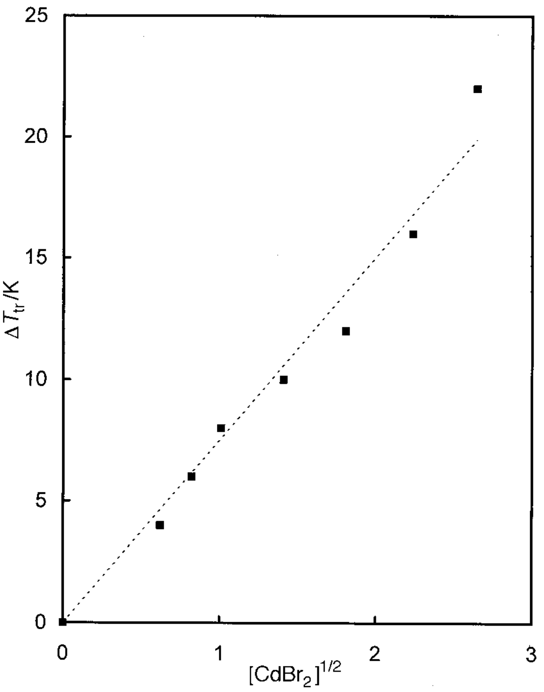

Fig. 2 Change in γ–β transition temperature as a function of dopant amount

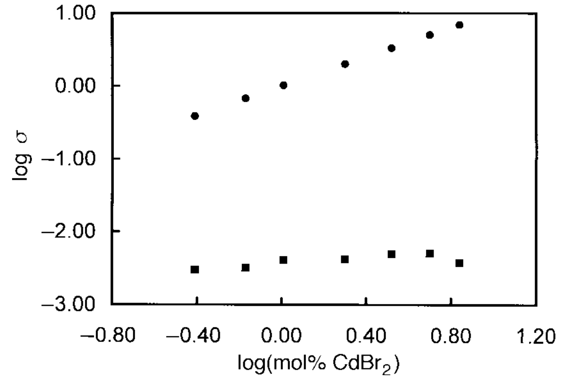

Fig. 3 Conductivity isotherms: ● 632 K; ■ 539 K

In the following, the experimental findings are discussed separately.

γ–β transition temperature

The difference of transition temperatures between doped and pure CuBr, was found to be a function of the square root of the dopant concentration, as shown in Fig. 2. As in the cases reported in ref. 2 and 3, this behavior may be qualitatively explained on the basis of the model proposed by Rice, Straessler and Toombs[5] which, in a simple form, states that a phase transition takes place when, with rising temperature, a critical defect concentration is reached which the structure can no longer accommodate. In the present case, as the dopant supplies the system with a number of extra defects, the critical defect concentration is reached at lower temperatures the higher the amount of dopant.

Conductivity increase in the γ phase

Fig. 3 shows the log conductivity in S cm^{-1} as a function of log [mol% $CdBr_2$] at two temperatures. In both cases, the slope is clearly lower than unity, in contrast to what should be expected, as both defect concentration and conductivity should be linear with amount of dopant. A lower slope at high dopant concentration could be related to the formation of large associates, forerunners of precipitation, as stated by Kroeger.[6] Furthermore, there is no evidence of a minimum in the conductivity isotherms, as found, for instance, for CuI[7] at dopant concentrations similar to the lowest used in the present case. In the literature, the existence of such a minimum is explained on the basis of the lower mobility of vacancies as

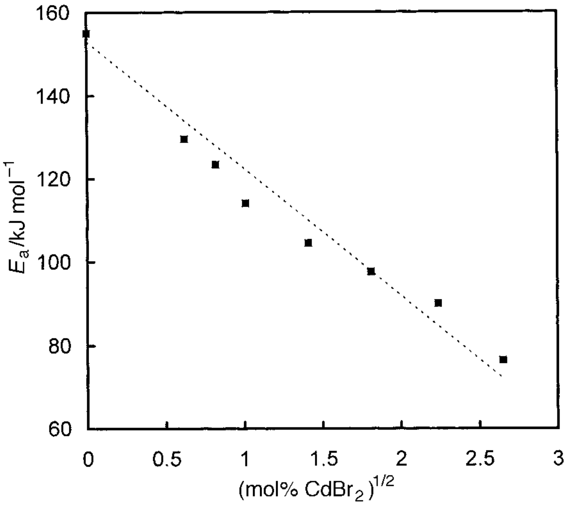

Fig. 4 Apparent activation energies for conductivity in the γ-phase as a function of the square root of dopant molar percentage

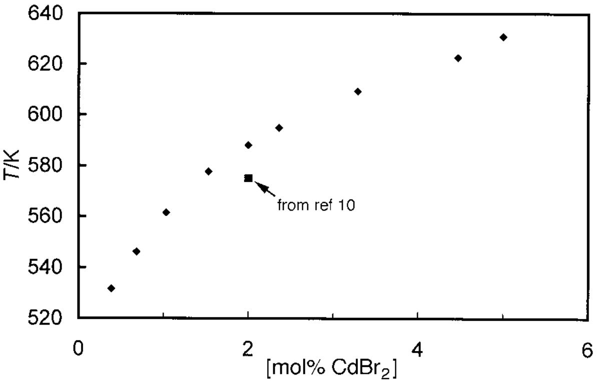

Fig. 5 Solubility curve for $CdBr_2$ into CuBr (■ value from ref. 10)

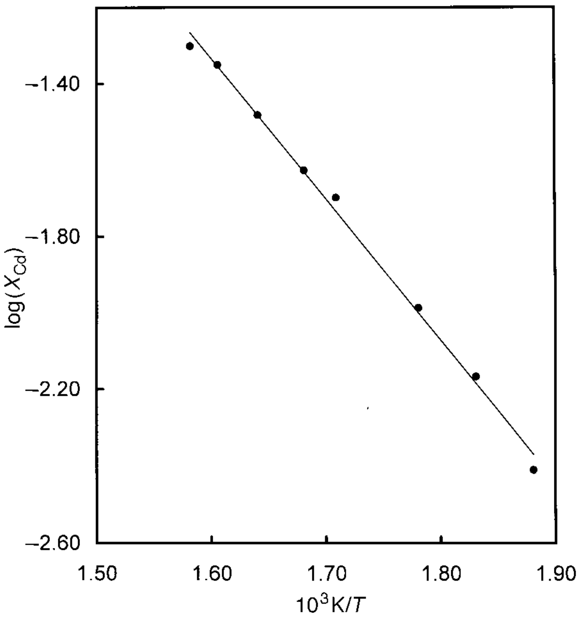

Fig. 6 Log of solubility *vs.* 1/*T*

compared to interstitials.[8] Thus, at dopant proportions when the dopant-fixed vacancy concentration is close to that of the intrinsic interstitials, its lower mobility causes a decrease in conductivity. As the dopant amount increases, the vacancy concentration reach higher values than those of the intrinsic defects and the conductivity starts to increase. This phenomenom it not evident in the present case, which points out to a lower concentration of intrinsic defects in CuBr than in CuI.

As for the apparent activation energy for conductivity in the γ phase, Fig. 4 shows a decrease from the value of 155 kJ mol^{-1} for pure CuBr following a square root dependence of dopant concentration, reaching *ca.* 75 kJ mol^{-1} at 7 mol%. This last figure may be approximately identified with the migration energy term as the contribution of intrinsic defects may be assumed as negligible. From these data a value of 160 kJ mol^{-1} is found for the formation energy of the Frenkel pair. Taking into account the experimental error involved, which can be estimated between 10 and 15% this figure is close to that earlier found[3] of 180 kJ mol^{-1} and the value of 145 kJ mol^{-1} reported by Safadi *et al.*[9] The coincidence is aceptable, taking into account that the compared values were obtained on the basis of different type of measurements.

The 'knee' in the Arrhenius plot of the γ phase

As pointed out above, the temperature of the knee increases with amount of dopant, thus reducing the temperature zone of promoted conductivity until it virtually disappears at 7 mol% $CdBr_2$. This effect, together with the above mentioned hint of precipitation, makes it reasonable to explain the knee as the solubility temperature of $CdBr_2$ in CuBr. On the other hand, SEM observations indicated phase separation between the components, at least at room temperature. In this way, the low temperature zone of the Arrhenius plots may be considered as the range in which $CdBr_2$ is precipitating as a separate phase and vacancies are being withdrawn, with a consequent decrease in the conductivity. Thus, the plot of the 'knee' temperatures as a function of dopant concentration, Fig. 5, may be considered as the solubility curve of cadmium bromide in copper(I) bromide. In the same plot the only value found in the literature, at 2% solubility at 300 °C, reported by Wagner is also shown.[10] Following the derivation made by Lidiard,[8] from the solubility curve, the corresponding values of the solution enthalpy and entropy can be obtained using the relationship:

$$x_{Cd} = \exp(\Delta S_{sol}/2R)\exp(-\Delta H_{sol}/2RT) \qquad (1)$$

where x_{Cd} is the molar fraction of cadmium bromide. Fig. 6 shows the logarithmic plot of the solubility data according to eqn. (1) from which the values of $\Delta S_{sol} = 175$ J mol^{-1} K^{-1} and $\Delta H_{sol} = 142$ kJ mol^{-1} were obtained. The large positive value of ΔH_{sol} is understandable taking into account the strain associated with the introduction of the aliovalent cation in the lattice.

Finally, as stated by Lidiard[8] the apparent activation energy from the Arrhenius plot in the precipitation zone should be equal to the sum of half the dissolution enthalpy plus the migration energy: $\Delta H_{sol}/2 + \Delta H_m$. The slopes of the Arrhenius plots corresponding to the different dopant amounts yielded an average activation energy of 147 ± 5 kJ mol^{-1}, which together with the obtained value of 142 kJ mol^{-1} for the dissolution enthalpy, gives a figure for the migration enthalpy of $\Delta H_m = 76$ kJ mol^{-1}, in good agreeement with both the above mentioned values and that of *ca.* 65 kJ mol^{-1} reported in ref. 3.

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