COMPOSITION-INDUCED FCC-BCC PHASE TRANSITION IN $Cu_{2-x}Ag_xSe$ SUPERIONIC SYSTEM

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FCC-BCC phase transition, which occurs in the high-temperature, superionic phase of $Cu_{2-x}Ag_xSe$ at x near 1.4, is described as a possible consequence of the energy increase of Cu^{2+} ions caused by dilution of Cu subsystem with Ag ions.

Introduction

Almost all simple Cu and Ag superionic conductors (SIC) consist of ordered, dense-packed FCC or BCC lattices of anions and disordered, liquid-like cation subsystems. FCC packing is characteristic for the high-temperature phases of copper salts while BCC packing predominates in the high-temperature phases of silver salts[1]. The nature of cation disorder and its consequences are quite different in FCC and BCC structures. Ionic conductivity, for example, is higher in BCC than in FCC phases. It has also smaller activation energy (about 4kJ/mol vs, about 16kJ/mol). FCC phases in addition usually exhibit the order-disorder transitions which do not appear in simple BCC salts. As it is known, these differences may be easily explained by the existence of two types of nonequivalent cation sites in FCC anion lattices and only one type of equivalent sites in BCC lattices. This work deals with a detailed picture of cation disorder in Cu_2Se (FCC) and Ag_2Se (BCC), and with the changes in it after the two compounds are mixed together giving the ternary compound $Cu_{2-x}Ag_xSe$. There is a very simple explanation of the FCC-BCC transition induced by variation of x in this picture

Cation disorder in Cu_2Se and Ag_2Se

A unit cell of Cu_2Se is found to contain 4 Se ions permanently fixed in FCC (a) sites, 4 Cu ions permanently fixed in the half of the tetrahedral (c) sites and 4 Cu ions more or less statistically distributed over the other half of tetrahedral (d), octahedral (b), and trigonal (e) sites[2,3]. More recent approaches to the structure of SIC

treat the e-sites only as transient sites, i.e. the sites where the cations dwell in their hopping path between b- and d-sites. Better to realize this type of disorder let us imagine for Cu_2Se a hypothetical structure with all mobile ions in d-sites (Fig.1a.). This is easily

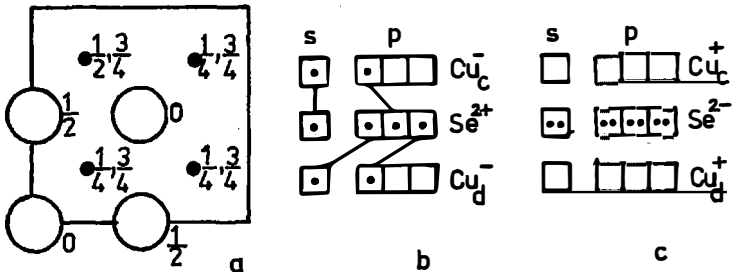

Fig.1. Unit cell, covalent and ionic bonding schemes of Cu_2Se in antifluorite structure. Open circles are Se ions, dots are Cu ions.

recognized as the antifluorite structure which is in Fig.1. represented by its bonding schemes. Since all tetrahedral sites are full and 4 Cu_c ions together with Se ions are found to form a perfectly ordered cage, the transition to a disordered state forces mobile Cu_d ions to occupy some other, crystallographically and energetically nonequivalent sites. Those are octahedral (b) sites. The transition, obviously, is possible only if the energy of Cu ions in transient sites is not too high. The situation is depicted in Fig.2. where all Cu_d ions are pla-

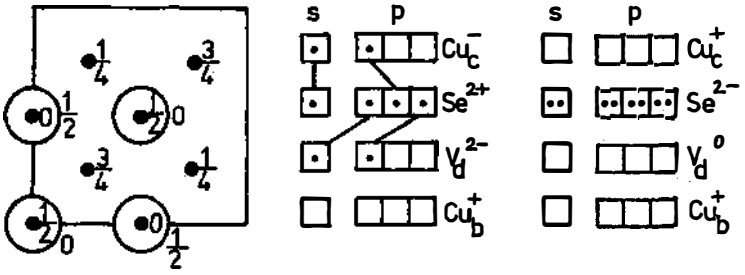

Fig.2. Unit cell, covalent and ionic bonding schemes of Cu_2Se with Cu_d ions in b-sites.

ced in b-sites. This picture should also be treated as hypothetical one. That in a real crystal consists of mixed states shown in Fig.1 and Fig.2. Four facts may be extracted from Fig.2:

i. Both the covalent and ionic bonding schemes suggest that Cu ions in b-sites are in oxidation state Cu_b^+. Their local orbitals are, however, unknown. For a possible situation see McOmber et al[4].

ii. To promote a Cu_d ion into a b-site the energy E_2 is necessary. It may be treated as the energy of the reaction $Cu_d^+ = V_d^o + Cu_b^+$ in which a Cu_b^+ ion and a vacancy V_d^o are created. E_2 should be a part of the activation energy E_i for the ionic conductivity.

iii. The bonding scheme for Cu ion in e-site is the same as represented for Cu ions in b-sites. Cu ions thus migrating through the crystal do not change their oxidation state (but change their orbitals). Production of a Cu_d ion in an e-site may be represented as the reaction $Cu_d^+ = V_d^o + Cu_e^+$. Its characteristic energy is the sum $E_1 + E_2$. We recognize in this sum the activation energy E_i. Its first part, E_1, is the activation energy for the mobility of Cu ions.

iv. Due to two types of sites with different energy one can expect the order-disorder transition in Cu_2Se (or generally in FCC structure). While this transition has indeed been found[5] in Cu_2Se, the real situation is far more complicated[6].

The cation disorder in Ag_2Se is quite different. A unit cell contains 2 Se ions in BCC sites and 4 Ag ions distributed over 12 tetrahedral (d), 6 octahedral (b) and 24 trigonal (h) sites[2]. As for some other silver salts, this distribution has been criticized regarding the possibility for Ag ions to reside in highly deformed octahedra (here an Ag ion is in fact twofold coordinated[7]). We shall treat therefore Ag_2Se as having only 12 tetrahedral and 24 trigonal, transient sites. A hypothetical ordered structure is shown in Fig.3. If the energy $E_1' + E_2'$

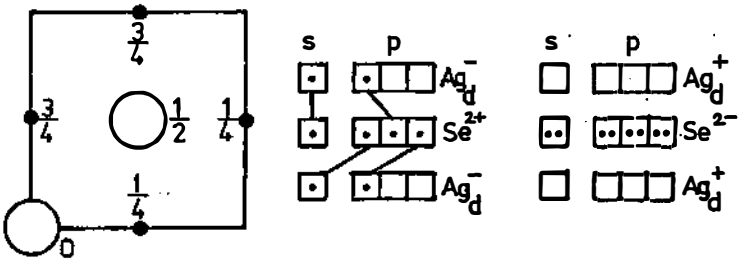

Fig.3. Unit cell, covalent and ionic bonding schemes of Ag_2Se in a hypothetical ordered state.

for the promotion of Ag_d ions into the transient sites or the energy of the reaction $A_g^+ = V_d^o + Ag_h^+$ is low enough, the system will transform to disordered state. But now only equivalent tetrahedral sites are avai-

lable. Thus the energy E_2' is equal to zero and $E_i'=E_1'$.

Despite equal bonding schemes the disorder in Cu_2Se and Ag_2Se is of two different types. While in Cu_2Se the paths through the crystal include alternate tetrahedra-octahedra, the paths in Ag_2Se are only series of tetrahedra. In both cases the polyhedra are connected by trigonal planes. Since E_i' is smaller than E_i, Ag_2Se is a "better" SIC. E_i may eventually be compared with E_i' only above the critical temperature for order-disorder transition where the population of b- and d-sites becomes equal.

Nonstoichiometry of Cu_2Se

Before a description of the cation disorder in mixed selenides we need some facts on the large stoichiometric deviations, $Cu_{2-y}Se$, a feature rarely found in other SIC. Simple supposition that each deficient copper atom comes from a b-site (it is at higher energy than a d-site) leads to the conclusion that a complex $V_b^-+Cu_b^{2+}$ appears instead of a missing Cu_b^+ ion. For the sake of electrical neutrality another Cu_b^+ ion in the neighbourhood of V_b vacancy is forced to transform to double ionized state. We have thus the reaction $Cu_b^+=V_b^o+Cu_b^+=V_b^-+Cu_b^{2+}$. Evidently, each Cu^{2+} ion may be treated as a hole bound to or released from a V_b vacancy. Stoichiometric deviations then, dope cuprous selenide giving it the properties of p-type semiconductor. Our scheme is in accordance with Rau's finding[8] that the reaction $V_b^o=V_b^-+h$ represents the principal doping mechanism in Cu_2S.

Various measurements[9] show that the energy of this reaction is very low or even zero. With almost all possible compositions the Fermi level lies deeply in the valence band giving a strong degeneracy and a high, temperature independent concentration of holes. Besides, cuprous selenide does not exist in exact stoichiometry. Despite nominal deviation y=0 the synthesis does not give Cu_2Se but $Cu_{2-ym}Se$. The equilibrium can evidently be reached with certain concentration of Cu^{2+} ions and with appropriate quantity of precipitated copper. The reaction $Cu_b^+=V_b^-+Cu_b^{2+}$ occurs spontaneously at y=0 but stops at y=ym. We may say again that its energy is zero but may be temperature dependent above y=ym. Electrochemical measurements by Valverde[10] made at 300°C showed that this energy indeed changes with y. It increases with increasing y.

FCC-BCC transition in mixed selenide

Being now familiar with the type of disorder in Cu_2Se and Ag_2Se and with the nonstoichiometry of Cu_2Se, let us turn towards the more general question of the possibility of Cu_2Se-like structures being

disordered in the same way as Ag_2Se structures, i.e. by the transition to a BCC lattice. Normally FCC-BCC transition does not occur in pure Cu_2Se since it is energetically unfavourable: the energy of reaction $Cu_d^+=V_d^o+Cu_b^+$, responsible for the disorder with b-sites, is evidently smaller than the latent heat of the hypothetical FCC-BCC transition. However, changing this energy relatioship in some way the mentioned transition may eventually become possible. We intend to show that the reaction $Cu_d^+=V_d^o+Cu_b^+$ is in close connection with reaction $Cu_b^+=V_b^-+Cu_b^{2+}$. In fact, the first reaction is strongly enhanced by the second. The jump of a Cu ion from d- to b-site in this picture seems simply to be a consequence of the transition of this ion into Cu^{2+} state. For this transition, as we have seen, small or no energy is needed.

At this point it is useful to mention our previous paper on the metal-nonmetal transition in $Cu_{2-x}Ag_xSe$[11]. By electrical conductivity measurements we showed that dilution of copper subsystem with silver leads to the gradual increase of acceptor energy owing to weakening interaction between them. At x=0.7-0.8 the metal-nonmetal transition occured, characterized by the change in sign of temperature coefficient of electrical conductivity. For x less than 0.7-0.8 the samples were metallic, while for x greater than 0.7-0.8 they were semiconducting. It is possible to estimate that at x near 1.4 the Fermi level is in the middle of the gap, reflecting the intrinsic properties of the crystal. The concentration of extrinsic holes (i.e. Cu^{2+} ions) falls therefore to zero at this composition.

We found that these results are in good agreeement with Valverde's finding[10] that the energy of Cu^{2+} ions increases with increasing content of silver. Indeed, in the mixed selenide each Cu^{2+} ion is more or less surrounded by Ag^+ ions. Owing to unfavourable transition of electrons from Ag^+ to Cu^{2+} ions, Cu^{2+} ions and V_b vacancies become localized. When the energy of Cu^{2+} ions become sufficiently high, the probability of their existence sharply decreases.

In the context of the mechanism just described the FCC-BCC transition has a very simple explanation. Since it occurs at x=1.38[10], which is almost the same value at which the conductivity measurements signalized the disappearence of Cu^{2+} ions, the two effects are evidently correlated. The correlation is easily understandable: dilution of Cu subsystem with Ag leads to the increase of the energy of reaction $Cu_b^+=V_b^-+Cu_b^{2+}$. The reaction thus becomes less and less probable. Since we treated it as a "booster" for the reaction $Cu_d^+=V_d^o+Cu_b^+$ this, in turn, also becomes improbable. To disorder its cation subsystem the mixed selenide chooses the only remaining way - The transition to BCC arrangement of anions.

The same effect has been observed in the mixed sulfide[12]. The FCC--BCC transition occurs in this system at x near 1.3 which is not far from the critical composition in the selenide. This suggests that the type of anions does not matter much in the effect. However, CuBr, which may appear as BCC and Ag_2Te which is of FCC structure do not support this suggestion. The study of these two exceptions may therefore give a deeper insight into the composition-induced phase transitions in copper and silver SIC.

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