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Superlattice ordering in digenite, $Cu_{2-x}S$

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We report a new sequence of superlattice ordering transitions in digenite-type crystals of $Cu_{2-x}S$. A long-period arrangement of the copper ions is found to undergo a spatial period doubling followed by a transition to an incommensurate phase at low temperatures. The results are discussed in terms of a mass-density-wave model describing the ordering of copper vacancies in the nearly stoichiometric case. A direct relationship between composition x and the superlattice period is predicted, leading to discrete equilibrium structures ($x = 0.11$ and 0.16), rather than continuous solid solutions.

The region of the copper sulfide system where the mineral digenite occurs, $Cu_{2-x}S$ $(0.05 < x < 0.26)$, is known to exhibit an intricate manifold of phases.[1] Over this range of compositions a rich variety of solid-state ordering phenomena have been reported including superlattice formation[2] and order-disorder transitions.[3] Such phenomena, which are often the result of competing interactions,[4] are of considerable current interest in their own right as well as from a technological standpoint.[1] Previous experimental attempts to elucidate the origin of this structural complexity in the copper chalcogenides have been frustrated by difficulties in sample preparation and accurate stoichiometry determination. To date, there is no comprehensive structural framework within which to discuss the interesting physical behavior of this class of materials.

In this paper we present new temperature-dependent x-ray scattering data on high-quality single crystals prepared from solid solutions covering the entire digenite range of composition. We will show that there are actually only two discrete equilibrium forms of digenite, corresponding to compositions $x = 0.11$ and $x = 0.16$, and that each composition derives from a particular *long-period ordering arrangement* of copper atoms within the sulfur matrix. The results suggest that the structural behavior in the region of the phase diagram spanning the stoichiometric compound Cu_2S (chalocite) may be described in terms of a mass-density-wave model. Application of this model, developed from earlier work by van Dyck, Conde, and Amelinckx,[5] allows a complete description of the digenite phase diagram to be made clarifying numerous conflicting results that have been reported in the literature.

The samples were prepared by reacting elemental sulfur and copper[6] in an evacuated quartz ampoule for several weeks at 700 °C. This single-zone method of growth produces from the vapor many small (0.1–1 mm) untwinned digenite crystals of two distinct compositions. Starting mixtures anywhere in the range $x = 0$ to $x = 1$ yielded useful crystals and samples of both digenite compositions frequently occurred in the same growth run as a result of phase separation. Note that in this method crystal growth takes place at temperatures which are some 400 °C below the solidus for the digenite composition range.

The compositions of individual crystals were carefully determined by a number of complementary methods. X-ray and Auger microprobe techniques were used in conjunction with the composition dependences of the lattice parameter and order-disorder transition temperature, both established previously from powder measurements.[3] The two stable compositions corresponding to the cubic digenite structure were determined to be $x = 0.15 \pm 0.03$ (blue-black in color) and $x = 0.09 \pm 0.03$ (grey-black).

The room-temperature structures of the two digenite compounds identified above correspond to three-dimensional N-fold commensurate superlattices such that the unit cell is a cube of side Na_0, where a_0 is the lattice spacing of the fcc sulfur framework[7,8] in which the copper atoms are situated [see inset (b) of Fig. 1]. Detailed x-ray diffractometer studies reveal an intriguing sequence of phase transitions associated with this long-period superlattice ordering. Here, we describe the behavior as a function of temperature starting with the high-temperature phase, which has lattice spacing a_0.

Previous studies using mainly electron diffraction[2] and photographic x-ray methods[9] have reported the emergence of superlattice peaks from diffuse streaks parallel to the $\langle 111 \rangle$ directions at temperatures somewhat less than 400 K. Figure 1 shows the results of the first quantitative diffractometer study of this order-disorder transition. The transition appears to be of second order and a power-law fit to the superlattice intensity (proportional to the square of the order parameter) yields an exponent β of 0.21 ± 0.02; we observe no thermal hysteresis at this transition. The value of β is considerably smaller than we expected for a three-dimensional (3D) order-disorder transition (cf. $\beta = 0.31$ for 3D Ising model) and is more typical of a two-dimensional exponent. We will discuss this point further in a moment.

The indexing of the diffraction pattern from which the particular data in Fig. 1 are derived indicates that a superlattice periodicity of $5a_0$ is established for $T < 353$ K. On further cooling, to approximately 295 K, a second phase transition is observed in which the superlattice periodicity *doubles* to precisely $10a_0$. This transition is distinctly first order in nature with thermal hysteresis of ~ 10 K [see inset (a) of Fig. 1] and has not been reported previously. Still further cooling drives the structure incommensurate at approximately 282 K, also a strongly first-order transition. The incommensurability of $\sim 1.5\%$ [see inset (c) of Fig. 1] remains constant to the lowest temperature of our measurements ($T = 30$ K). The latter, unreported, transitions may correspond to anomalies recently observed in specific heat measurements on powdered copper sulfide.[10]

The x-ray measurements above refer to digenite crystals with composition $x \approx 0.15$. A similar sequence of transitions is encountered for crystals which grow with the other

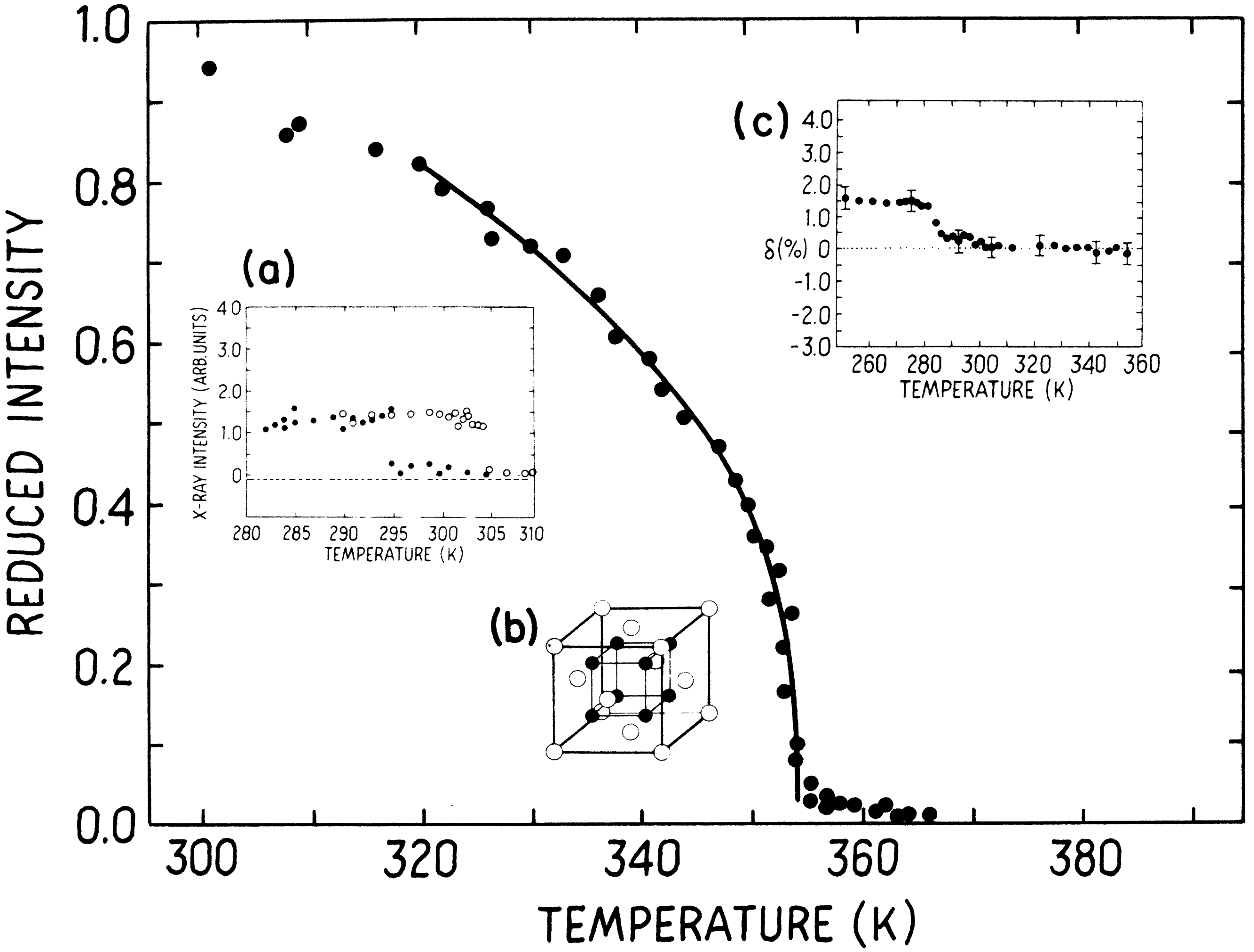

FIG. 1. Order-disorder transition in $5a_0$ digenite, $Cu_{1.84}S$. The solid line is a power-law fit with $2\beta = 0.42$, $T_m = 353$ K. Insets: (a) First-order doubling transition, $5a_0 \leftrightarrow 10a_0$; open circles are the heating cycle; full circles represent cooling. The intensity of the $2\pi/10a_0$ (15,15,15) reflection of $Cu_{1.84}S$ is shown. (b) Antifluorite unit cell for digenite; open circles represent sulfur; solid dots represent copper sites. (c) Commensurate-incommensurate transition in $10a_0$ sample. δ is the relative incommensurability. The transition is first order. The behavior of the $2\pi/10a_0$ (18,18,18) peak is shown.

stable composition, $x \approx 0.09$. In this case, the ordering sequence is $a_0 \rightarrow 6a_0 \rightarrow 12a_0 \rightarrow$ incommensurate. Also, the transition temperatures are all shifted up by 60 K, as might be expected from the stiffening of elastic constants as the structure approaches stoichiometry.

The existence of discrete compounds (rather than a continuous solid solution), the ordered structures of which correspond to particular long-period superlattices, supports a mass-density-wave (MDW) description for the ordering. It is clear that the sulfur matrix remains unchanged[7] throughout the above sequence of transitions so that it is the ordering of copper ions which is involved in the observed behavior. In the analysis of our results we therefore employ a structural model based on the ordering of vacancies within the antifluorite configuration of copper ions in the cubic digenite structure (see Fig. 2). As first pointed out by van Dyck *et al.*,[5] the copper vacancies must be grouped preferentially on (111) planes in order to satisfy the observed distribution of diffuse scattering. In the high-

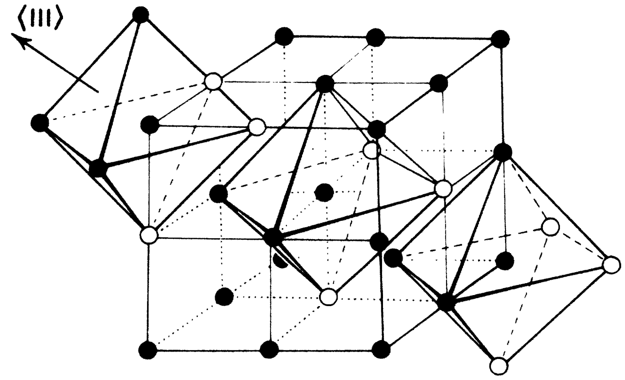

FIG. 2. Depiction of MDW (ordered vacancies) in the copper sublattice of $Cu_{2-x}S$. The full circles represent filled copper sites and open circles denote vacancies. Sulfur atoms not shown (see Fig. 1, inset).

temperature phase three copper ions would be shared equally among all six of the octahedral sites (see Fig. 2) by hopping between them. Figure 3 illustrates the way in which an N-fold three-dimensional superlattice can be constructed from the $\langle 111 \rangle$ copper MDW shown in Fig. 2. The construction begins with an $N \times N \times N$ supercube, where each small block is a sulfur fcc unit cell (a_0^3); the cubic symmetry requires placement of vacancies along all equivalent $\langle 111 \rangle$ directions of the $N \times N \times N$ supercube. The structure is best viewed as an otherwise filled copper sublattice threaded with chains of ordered vacancies along the $\langle 111 \rangle$ axes. It is easily seen from Fig. 3 that each N-fold superlattice will correspond to a definite composition $Cu_{2-x}S$. The predicted stoichiometries for the $5a_0$ and $6a_0$ structures are $x = 0.16$ and $x = 0.11$, respectively, in excellent agreement with the observed values.

The MDW model outlined here, which will be described in further detail in a forthcoming publication,[11] can also account for other features of the x-ray data. The order-disorder transition is interpreted as a change to a uniform occupancy of the sites at the vertices of the octahedra shown in Fig. 2. The diffuse scattering from such a configuration has been predicted[5] to give rise to Lorentzian line shapes, in agreement with what we observe for $T > T_m$.[11] We also suggest that the reduced dimensionality of this chainlike configuration gives rise to crossover effects and lowering of the effective critical exponent β, i.e., it appears that we are unable experimentally to approach T_m sufficiently closely to access the full three dimensionality of the ordering. Moreover, the period doubling transition (e.g., $5a_0$ to $10a_0$) can also be simply interpreted within the MDW model. A careful examination of the configuration of vacancies in Fig. 2 reveals that there is a twofold degeneracy in how the vacancies in a particular antifluorite cube can be placed. With the arrangement of vacancies alternating between these two states, a spatial period doubling naturally occurs. Thus the period doubling is interpreted as a breaking of the degeneracy as the vacancies order.

It is interesting that the lowest-temperature configuration of the MDW is not an ordered commensurate superlattice. Possibly, at low temperatures, the structure becomes unstable to some still higher-order superlattice configurations reminiscent of the devil's staircase[4] but these cannot form an ordered arrangement for kinetic reasons. High-resolution electron microscopy[5] has shown evidence that coexistence of $5a_0$ and $6a_0$ orderings can give rise to an incommensurate structure. We suggest that a similar mechanism may be operative in the present case; for example, a $10a_0$ periodicity mixed with some still higher-order superstructure could mimic a weakly incommensurate phase such as that observed. Further investigations are required to elucidate the nature of the commensurate-incommensurate transition.

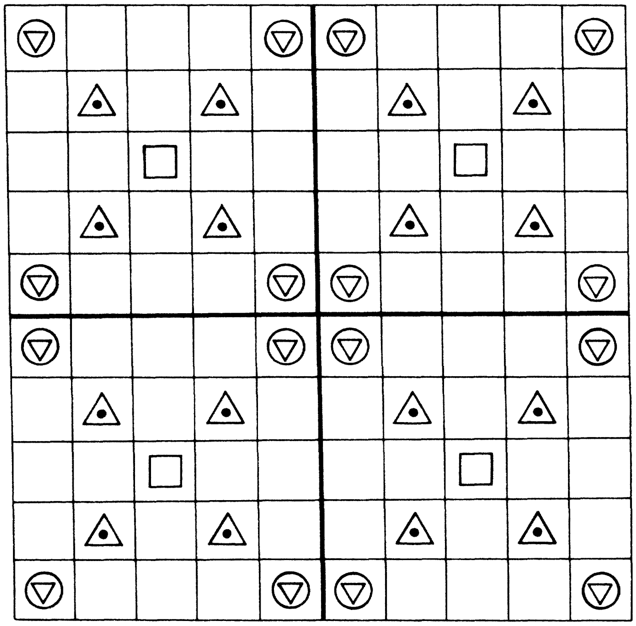

FIG. 3. {100} projection of the three-dimensional superlattice structure of $5a_0$ digenite. The superposed symbols 0, Δ, □, ●, and ∇ represent the placement of copper vacancies on levels 1–5 of the $5 \times 5 \times 5$ cell outlined in heavy lines. Chains of vacancies, as shown in Fig. 2, run parallel to the $\langle 111 \rangle$ axes.

The MDW model presented here holds promise for interpretation of other complex structures in the copper sulfide[12] and copper selenide[13] systems. For example, we believe that many of the unusual phases reported in $Cu_{2-x}S$ can be obtained by simple rotations[11] of the superlattice translation vectors and may be the result of the very sluggish kinetics of ordering in these materials.

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