JOURNAL OF SOLID STATE CHEMISTRY 60, 29–40 (1985)

Solid State Reactions in the Quasibinary System Ga_2Te_3/CdTe

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Received December 4, 1984; in revised form March 14, 1985

The quasibinary system Ga_2Te_3/CdTe was investigated in order to derive its thermodynamic and kinetic properties. The phase diagram between 750 and 1000 K was obtained from powder X-ray photographs. The results suggest an order–disorder transition in the phase $CdGa_2Te_4$. Reactions were carried out between single crystals of Ga_2Te_3 and CdTe, between CdTe and $CdGa_2T_4$, and between Ga_2Te_3 and $CdGa_2Te_4$. Reaction profiles and growth kinetics were determined by electron microprobe analysis. The morphology of the reaction layer is discussed with respect to the phase diagram and the varying concentration of structural vacancies and their ordering in the product phase $CdGa_2Te_4$.

I. Introduction

The system CdTe/Ga_2Te_3 can be regarded as a quasibinary section through the ternary system Cd/Ga/Te (Fig. 1). Among the different tellurides of gallium the compound Ga_2Te_3 (*1–5*) is the only one that crystallizes in the same lattice-type as CdTe. Both crystals (Ga_2Te_3 and CdTe) are characterized by a cubic face-centered tellurium sublattice. However, in the metal sublattice of the Ga_2Te_3 compound only two out of three available lattice sites are occupied by atoms. At high temperatures the Ga atoms are distributed statistically on the available sites. The lattice of this disordered Ga_2Te_3 crystal is called the defect zincblende lattice. CdTe on the other hand builds up the normal zincblende structure. With decreasing temperature the metal sublattice vacancies of Ga_2Te_3 are expected to become ordered, leading to a special type of superstructure (*6–8*).

Whereas at low temperatures, in the ordered phase, the vacancies can be considered as interstitial sites of the superstructure, they are part of the metal sublattice in the disordered, high-temperature structure and are called structural vacancies of the defect zincblende lattice. To indicate that both CdTe and Ga_2Te_3 belong to the same thermodynamic phase CdTe will be designated as Cd_3Te_3, by analogy to Ga_2Te_3.

The properties relevant to the miscibility of the binary components exhibit considerable differences:

Melting point [T(K)]
  1370 (CdTe); 1063 (Ga_2Te_3);
Lattice constant [a(pm)]
  647.7 (CdTe); 590.4 (Ga_2Te_3);
Electronegativity (*9*)
  0.83 (Cd); 1.13 (Ga); 1.47 (Te).

Therefore, despite the same lattice type of the two components, a broad miscibility gap is to be expected. Furthermore, it is known (*10*) that CdTe and Ga_2Te_3 form a ternary product phase of composition $CdGa_2Te_4$, which can also be regarded as a slightly distorted superstructure of the

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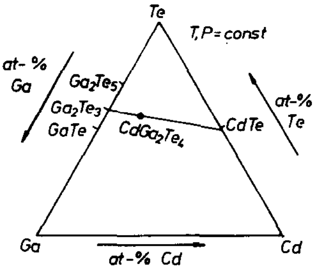


FIG. 1. The ternary system Ga/Cd/Te.

zincblende lattice where one-fourth of the original cation sites are vacant. However, these vacant sites act not as defects in the metal sublattice but as interstitial sites of the superstructure.

From measurements of the lattice constants by a Guinier X-ray camera on polycrystalline samples the thermodynamic phase diagram of the quasibinary system was derived. To investigate the solid-state reactions in this system, couples of single crystals of the reaction components were used. The reaction zones formed during annealing at high temperatures were investigated by electron microprobe techniques and by optical microscopy.

II. Experimental Details

Synthesis of Binary Components

The binary compounds were synthesized from the pure elements (Ga 99.999%, Cd 99.999% from Koch Light Labs; Te 99.9998% from Ventron). As Ga_2Te_3 cannot be purified by sublimation, tellurium was distilled before use in the synthesis of Ga_2Te_3.

CdTe was synthesized by heating a stoichiometric mixture of the elements in an evacuated quartz ampoule up to 1373 K. Then the CdTe was sublimed twice in a dynamic vacuum and thereafter reannealed at 873 K for another 8 hr in a dynamic vacuum. CdTe produced in this way has a composition corresponding to the minimal vapor pressure.

Crystal Growth

CdTe and Ga_2Te_3 crystals were grown from the melt by the Bridgman method.

Small crystals of $CdGa_2Te_4$ were obtained by sintering and by recrystallisation of an equimolar mixture of CdTe and Ga_2Te_3. Some of the CdTe and Ga_2Te_3 crystals were annealed for 8 hr in a dynamic vacuum (773 K for Ga_2Te_3, 873 K for CdTe) to obtain a composition corresponding to the minimal vapor pressure. Another portion of the crystals was annealed in evacuated quartz ampoules together with an excess of one of the pure elements of the compound. Crystals prepared in this manner (intrinsically doped) are metal-saturated or Te-saturated, depending on the added element (Table I).

III. Investigation of the Phase Diagram Cd_3Te_3/Ga_2Te_3

(1). *X-Ray Diffraction Measurements*

The lattice constants determined by the Guinier method on quenched samples at room temperature are used for the investigation of the phase diagram.

Samples with an overall composition belonging to a two-phase region of the phase diagram show the X-ray line sets of both

TABLE I

CONDITIONS FOR DOPING OF CdTe AND Ga_2Te_3 CRYSTALS[a]

Material	T (K)	Overall composition of ampoule content	Composition of doping mixture	Annealing time
Ga_2Te_3 (Ga)	773	42 at% Ga/58 at% Te	GaTe + Ga_2Te_3	14d
Ga_2Te_3 (Te)	773	38 at% Ga/62 at% Te	Ga_2Te_3 + Te	
CdTe (Cd)	973	51 at% Cd/49 at% Te	CdTe + Cd	
CdTe (Te)	973	49 at% Cd/51 at% Te	CdTe + Te	

[a] The element in brackets indicates the component the crystal will be saturated with after annealing.

phases coexisting at thermodynamic equilibrium.

To ensure that lattice constants calculated from the X-ray reflections of quenched samples really correspond to the high temperature equilibrium, the samples were prepared in two ways.

(a) Samples in Set I were first homogenized at high temperature, and then cooled to the equilibrium temperature

(b) For samples of Set II the temperature was not raised past the equilibrium temperature.

After equilibration the samples for both Sets I and II were quenched by dropping the ampoules into water.

The equilibration temperatures and times are specified in Table II. Both sets of samples yield sharp X-ray lines; for a given overall composition the mean lattice constants of samples in both sets differ by less than ±1 pm.

Therefore one can be sure that thermodynamic equilibrium was established, and that equilibrium compositions can be preserved by quenching.

At 773 K (Fig. 2a) all samples with a Ga_2Te_3 content up to 70 mole% yield the same value for the cubic lattice constant as pure CdTe. Furthermore, all samples with an overall composition up to 86 mole% Ga_2Te_3 show the presence of the compound $CdGa_2Te_4$. Since all samples yield the same values for the lattice constants *a* and *c* of the tetragonal $CdGa_2Te_4$ compound, we conclude that at 773 K this ternary phase does not show a measurable solubility for CdTe or Ga_2Te_3.

TABLE II

Equilibration Conditions for the Polycrystalline Samples of Sets I and II

	T (K)	Time (d)
Set 1	973	46
	873	70
	773	72
Set 2	773	75
	873	92
	973	19

Ga_2Te_3-rich samples with $x_{Ga_2Te_3} \geqq 0.9$ exhibit only a single set of lines. Here, the cubic lattice constant decreases continuously to that of pure Ga_2Te_3 ($a = 590.4$ pm). Whereas, at 773 K, CdTe does not show any measurable solubility for Ga_2Te_3, the solubility of Cd_3Te_3 in Ga_2Te_3 at this temperature already amounts to 10 mole%.

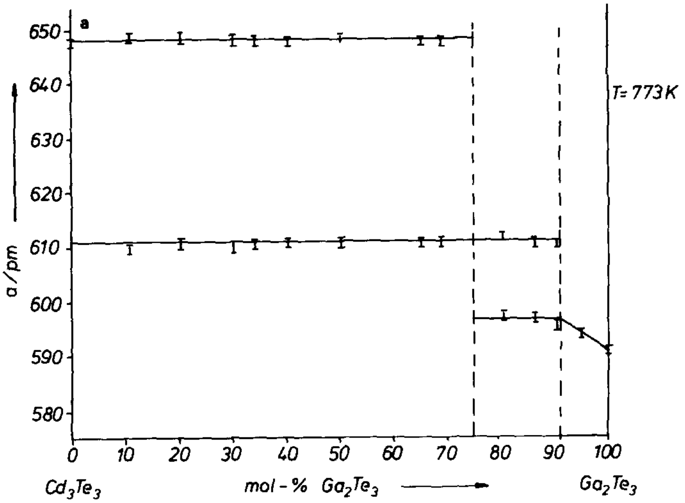
With increasing temperature Ga_2Te_3 becomes soluble in CdTe and this solubility increases much faster than the solubility of CdTe in Ga_2Te_3.

Above 900 K (Fig. 2*c*) the product phase $CdGa_2Te_4$ also shows measurable solubility for CdTe and Ga_2Te_3. Deviations from the stoichiometric composition at higher temperature produce different values of the tetragonal lattice constants depending on the type of solid solution (either CdTe- or Ga_2Te_3-rich) with which the product phase has been equilibrated.

At 873 K (Fig. 2b) apparently a new phase is formed with a small existence region on both sides of the composition $x_{Ga_2Te_3} = \frac{3}{8}$. This composition corresponds to a phase with formula $Cd_5Ga_2Te_8$, but apart from a shift of lattice constant, the X-ray lines of this phase are not different from those of CdTe. Above 900 K this isolated phase can no longer be detected, but now the solubility of Ga_2Te_3 in Cd_3Te_3 extends up to 50 mole%. In the region $0.1 < x_{Ga_2Te_3} < 0.5$ the cubic lattice constant changes linearly, according to Vegard's rule

$$x_{Ga_2Te_3} = -1.70 \times 10^{-2} \times a(\mathrm{pm}) + 11.04. \quad (1)$$

In samples for which $x_{Ga_2Te_3} < 0.1$ the lattice constant decreases much more slowly with increasing $x_{Ga_2Te_3}$ than expected from


a
T= 773 K
a /pm
650
640
630
620
610
600
590
580
0
10
20
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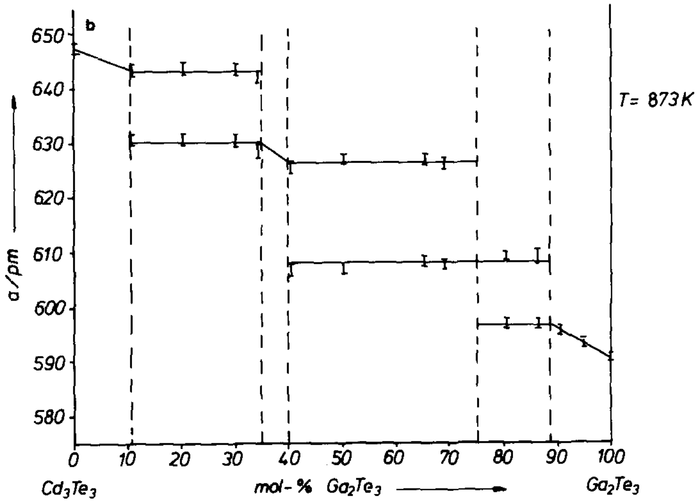
50
60
70
80
90
100
Cd3Te3
mol - % Ga2Te3
Ga2Te3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T= 873 K
a /pm
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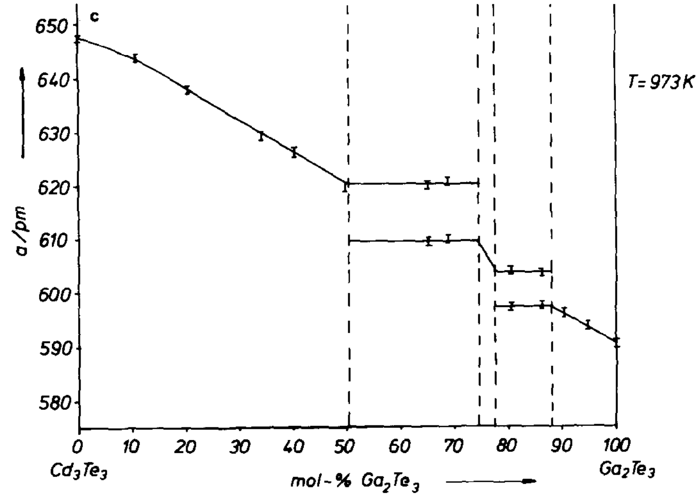
Cd3Te3
mol - % Ga2Te3
Ga2Te3


c
T= 973 K
a /pm
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40
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60
70
80
90
100
Cd3Te3
mol - % Ga2Te3
Ga2Te3

Eq. (1). This can be explained by a stability of the lattice against small amounts of foreign atoms. Alloying small quantities of Ga_2Te_3 may be regarded as a type of doping, for which the distance between the defects is still so great that the strain introduced by the defects can be balanced out locally by the lattice. This persistence of the lattice against small amounts of foreign atoms has also been observed in other tetrahedrally coordinated systems, e.g., GaAs/GaSb (*11*) or GaP/InP (*12*).

Though the lattice constants a and c of the $CdGa_2Te_4$ phase have been measured on quenched samples at room temperature they show a measurable dependence on the equilibration temperature. The constant a decreases whereas the constant c increases with increasing equilibration temperature (Table III).

TABLE III

DEPENDENCE OF THE LATTICE CONSTANTS OF $CdGa_2Te_4$ ON THE EQUILIBRIUM TEMPERATURE

	T (K)		
	773	873	973
a (pm)	610	608	605
c (pm)	1186	1188	1201
c/a	1.944	1.954	1.985

It is not easy to understand why the c/a ratio of the product phase at temperatures below 900 K is distinctly less than 2, but approaches 2 when the equilibration temperature is increased. Samples of equal composition, quenched to the same temperature, and showing no phase transformation, should yield the same values for the lattice constants. The observed behavior may be understood by assuming that a diffusion-controlled order–disorder transformation of the defect chalcopyrite lattice sets in at higher temperatures.

Because of the difference in electronegativities between Cd and Ga on one hand and the Te on the other hand the Coulomb interaction between the lattice elements of the zincblende structure will contribute significantly to the chemical bond. Thus a cation vacancy will induce a repulsion between the Te anions surrounding this vacanacy and thereby contribute to a small expansion of the lattice. In the ordered $CdGa_2Te_4$ phase these vacancies are arranged in the 001-planes such that all vanacies within one plane are equidistant (*10*). Whereas this distance is equal to the lattice constant a, the shortest distance to the vacancies in neighboring 001 planes is $d = a\sqrt{\frac{3}{2}}$.

Therefore the defect chalcopyrite structure has a higher density of vacancies within the base plane than along the c axis. For that reason a lattice distortion caused by the ordered vacancies yields a ratio of $c/a < 2$ for the tetragonal phase.

Increasing disorder of the vacancies with increasing temperature should decrease the lattice distortion because the vacancies will then be distributed more and more statistically over the cation sublattice. The mean vacancy density in the 001 planes will also decrease and thus the distortion of the lattice caused by the anisotropy of the vacancy distribution will likewise diminish. The axial ratios $c/a \neq 2$ in tetrahedrally coordinated chalcogenides were also investigated by Robbins *et al.* (*13*). The phase diagram shown in Fig. 3 was obtained from the temperature and composition dependence of the lattice constants. The shape of the equilibrium curve of the CdTe-rich zincblende phase can be explained by a superposition of a purely thermodynamic miscibility gap within the CdTe-rich solid solution and of a structural miscibility gap between the zincblende and the defect chal-

FIG. 2. Lattice constants as determined from Set II: (a) T = 773 K; (b) T = 873 K; (c) T = 973 K.

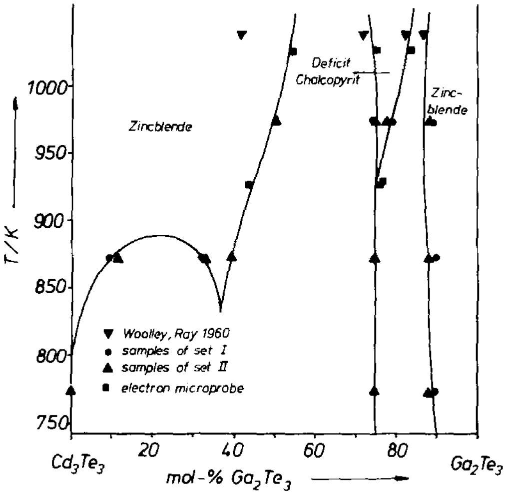

FIG. 3. Phase diagram of the quasibinary system Ga_2Te_3/Cd_3Te_3 in the temperature region $750 K < T < 1050 K$. (▼): data taken from literature (*15*); (■): data calculated from microprobe analysis of reaction couples; (●, ▲): data calculated from X-ray diffraction patterns of sample Sets I and II.

copyrite lattice. The relative maximum of the equilibrium curve at about 20% Ga_2Te_3 corresponds to the critical point of demixing of the CdTe-rich phase.

The Ga_2Te_3-rich solid solutions at high temperatures crystallize in the so-called defect zincblende lattice with one-third of the metal sublattice sites as structural vacancies. The X-ray diffraction patterns of these solid solutions indicate that an ordering process starts below 700 K. From the weak additional lines observed in the X-ray diagrams it was not possible to determine the superstructure of the ordered phase.

IV. Reactions in the System $CdTe/Ga_2Te_3$

(*a*) *Reactions between the Binary Components*

The reactions were carried out between crystals whose polished surfaces were pressed against each other within a matrix of polycrystalline CdTe at a pressure of approximately 10 kbar.

Reactions between CdTe and Ga_2Te_3 crystals were carried out in the temperature range

$$773 \text{ K} < T < 1023 \text{ K}$$

with reaction times ranging between 15 min and 400 hr, depending on temperature.

Investigations of the influence of intrinsic doping on the growth process of the product layers were carried out at 873 K. The occurrence of two product layers in this temperature region permits parallel measurements of the two growth rates, which are expected to be influenced by intrinsic doping either in their absolute values or in their ratio.

773 K. The X-ray intensity profiles for Cd and Ga measured with an electron microprobe (Fig. 4) clearly show the formation of a $CdGa_2Te_4$ product layer. In the micrograph (Fig. 5) this layer forms a bright stripe. At the Ga_2Te_3-rich border of this layer a narrow groove has been formed.

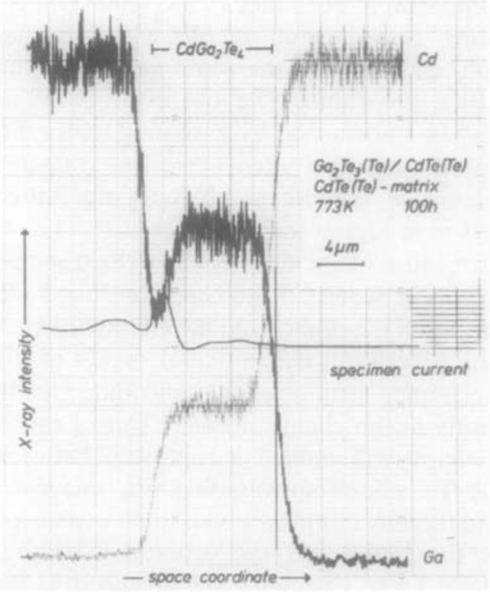

FIG. 4. X-Ray intensity profiles of Cd and Ga for the cation exchange between chalcogen saturated CdTe and Ga_2Te_3 crystals (100 hr, 773 K).

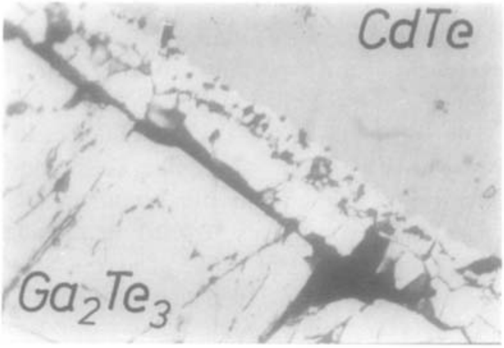

FIG. 5. Micrograph of the reaction zone between chalcogen-saturated CdTe and Ga_2Te_3 crystals (408 hr, 773 K). Magnification: 500 ×. The product layer $CdGa_2Te_4$ is situated between the groove and the CdTe crystal.

873 K. At this temperature the Cd- and Ga-profiles (Fig. 6) show the formation of two product layers, as one would expect from the phase diagram. The narrow groove between the $CdGa_2Te_4$ layer and the Ga_2Te_3-rich solid solution region is reflected in the minimum in the Ga profile as well as in the maximum of the sample current. In the CdTe-rich product layer the Cd and Ga intensities change nearly linearly across the layer. The porous zone within this layer—clearly shown by the micrograph (Fig. 7)—is more pronounced the longer the annealing time.

In the metal-saturated reaction couples these pores often aggregate into channels extending to the phase boundaries.

Whereas in the CdTe-rich solid solution the Ga-intensity decreases gradually in a flat profile to zero intensity, in the Ga_2Te_3-rich solid solution, for annealing times greater than 8 hr, the Cd intensity does not reach the zero level even at a distance of 100 μm from the phase boundary. For very long annealing times the Ga_2Te_3 crystal even becomes saturated with CdTe, indicating a high interdiffusion coefficient for Ga and Cd in the Ga_2Te_3 lattice.

The comparison between the thickness growth of the $CdGa_2Te_4$ product layer and the CdTe-rich product layer (Figs. 8a and b) shows no significant difference between metal-saturated samples and samples of minimum vapor pressure. Thus, there is little difference between compositions of differently treated samples. However, for Te-saturated samples the $CdGa_2Te_4$ layer growth becomes retarded whereas growth of the CdTe-rich product layer becomes ac-

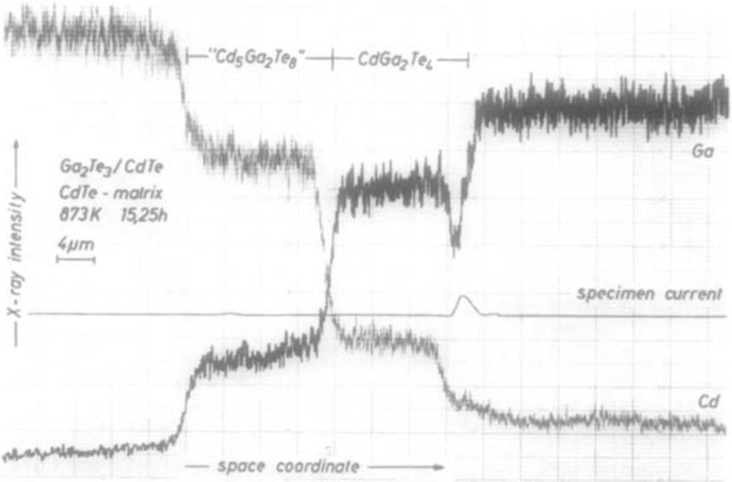

FIG. 6. X-Ray intensity profiles of Ga and Cd for the cation exchange between CdTe and Ga_2Te_3 crystals (15.3 hr, 873 K).

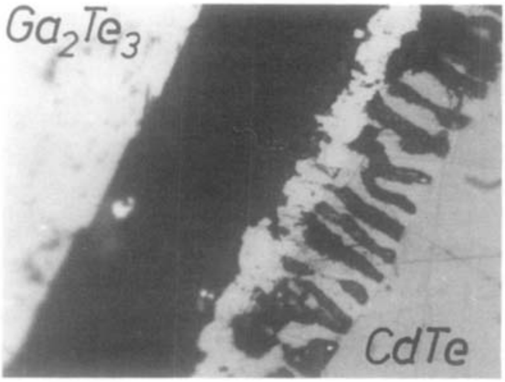

FIG. 7. Micrograph of the reaction zone between metal-saturated CdTe and Ga_2Te_3 crystals (15.5 hr, 873 K). Magnification: 1000×. The product layer $CdGa_2Te_4$ forms a bright stripe between the groove and the porous zone. The layer "$Cd_5Ga_2Te_8$" is situated in the porous zone.

celerated compared to the metal saturated samples.

923 K. At this temperature the phase boundary between the $Cd_5Ga_2Te_8$ layer and the CdTe-rich solid solution has been eliminated. Rather, continuously running Cd and Ga profiles are formed, the steepest sections of which are situated in a composition region corresponding to the critical point of the miscibility gap.

The solubility of Ga_2Te_3 in $CdGa_2Te_4$ increases with increasing temperature, and the groove shifts from the boundary between the two phases toward increasing CdTe-content. At 923 K the groove is situated near the CdTe-rich phase boundary of the $CdGa_2Te_4$ layer.

The metal interdiffusion within the Ga_2Te_3 crystal does not increase measurably even at higher temperatures. Thus at 923 K for an annealing time of 6 hr the Cd intensity inside the Ga_2Te_3 crystal reaches zero level, whereas for a comparable layer thickness at lower temperatures and higher annealing times the Ga_2Te_3 crystal is nearly saturated with CdTe.

973 K. The most significant differences in reaction behavior at lower temperatures are the flattening of diffusion profiles within the CdTe-rich solid solution, and the gradual disappearance of the groove (Fig. 9).

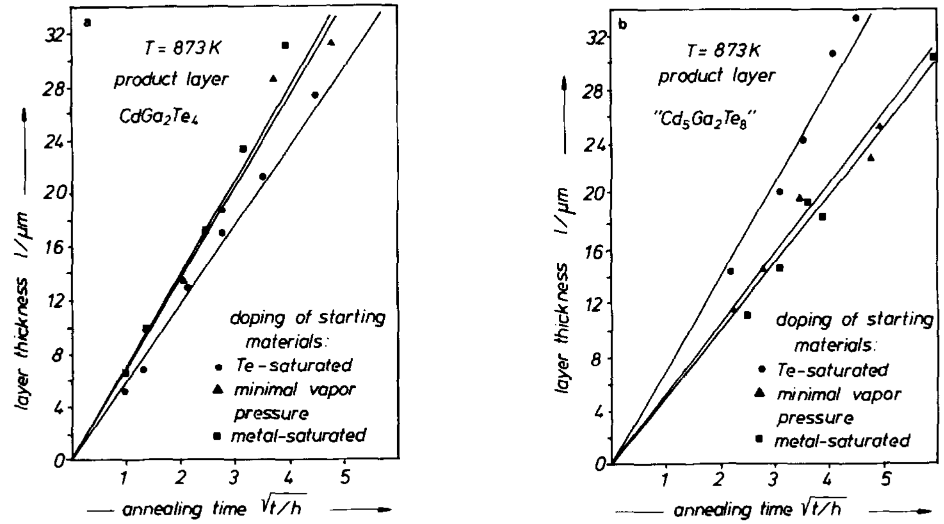

FIG. 8. Thickness growth of the product layers for reactions between Ga_2Te_3 and CdTe crystals at $T = 873$ K: (a) growth of $CdGa_2Te_4$; (b) growth of "$Cd_5Ga_2Te_8$." The thicknesses were determined by microprobe analysis and plotted against the square root of the annealing time, assuming parabolic thickness growth.

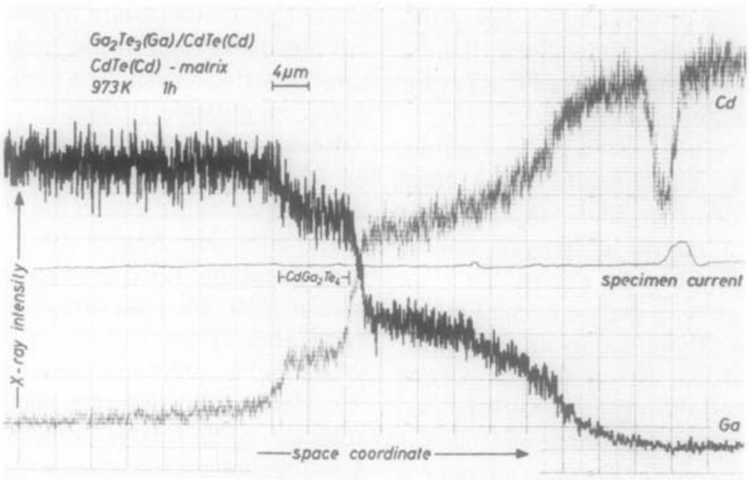

FIG. 9. X-Ray intensity profiles of Ga and Cd for the cation exchange between metal saturated CdTe and Ga_2Te_3 crystals (1 hr, 973 K).

1023 K. At this highest reaction temperature the existence region of the $CdGa_2Te_4$ phase extends from about 73 to 83 mole% of Ga_2Te_3. The solubility of Ga_2Te_3 in Cd_3Te_3 has also increased up to 55 mole%. In spite of the very thick reaction layers (up to 100 μm), related to the short annealing times of less than 1 hr, the interdiffusion in the Ga_2Te_3 crystal does not increase perceptibly.

(*b*) *Reactions between Crystals of the Ternary Phase $CdGa_2Te_4$ and One of the Binary Phases*

$CdGa_2Te_4$ + CdTe; 873 K. According to the phase diagram (Fig. 3), a single product layer with a small composition range near by $Cd_5Ga_2Te_8$ is formed in this reaction (Fig. 10). In contrast to the reaction between CdTe and Ga_2Te_3, no porous zone is

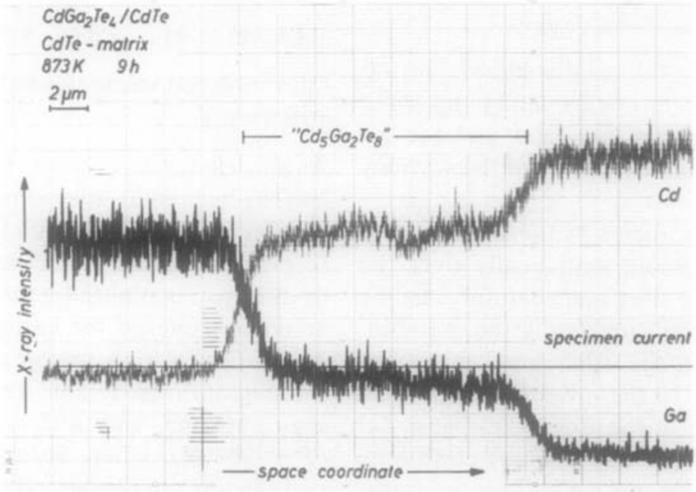

FIG. 10. X-Ray intensity profiles of Ga and Cd for the cation exchange between CdTe and $CdGa_2Te_4$ crystals (9 hr, 873 K).

formed within the product layer. The product layer growth is distinctly slower than in the reaction between CdTe and Ga_2Te_3 for comparable conditions.

$CdGa_2Te_4$ + Ga_2Te_3; 873 K. In contrast to the preceding experiments the reaction couples of $CdGa_2Te_4$ and Ga_2Te_3 were embedded in a matrix of polycrystalline Ga_2Te_3.

As no product layer can be formed in this reaction system, there is only an interdiffusion of Cd and Ga. No groove or porous zones are formed during this diffusion process. During an annealing time of 10 hr Cd penetrates into the Ga_2Te_3 crystal over a distance of more than 600 μm. On the other hand the interdiffusion in the $CdGa_2Te_4$ phase is nearly negligible.

V. Discussion

The interdiffusion in the metal sublattice of the quasibinary system Cd_3Te_3/Ga_2Te_3 is characterized by the fact that the quasibinary character only can be preserved if the difference between the Cd and Ga fluxes can be compensated by a vacancy flux

$$J_{Cd} = J_{Ga} + J_V.$$

It follows that in the solid solutions the vacancy flux always occurs along the same direction as the Ga flux, and that the Ga flux must be about twice that of the vacancy flux.

Structural vacancies in these solid solutions are distributed statistically over the metal sublattice sites and therefore can be treated as defects supporting the metal interdiffusion. On the other hand the structural vacancies in the ordered defect chalcopyrite lattice of the $CdGa_2Te_4$ phase act as interstitial sites; they can only contribute to the diffusion process if cations are transferred onto those interstitial sites.

Therefore, within the ordered $CdGa_2Te_4$ phase fewer defects are available for metal interdiffusion than in the neighboring solid solutions that crystallize in the disordered defect zincblende structure.

Because of the difference in structural vacancies in ordered and disordered lattices the interdiffusion in the ordered lattice is the rate determining step of the solid-state reaction. As it is energetically more favorable to fill interstitial vacancies with metal atoms than to produce new vacancies in the metal sublattice the prevailing defect disorder in the $CdGa_2Te_4$ phase is an interstitialcy. As in related compounds with ordered structural vacancies, such as In_2Te_3 or Ga_2Se_3, it is difficult to produce such ordered compounds with an excess of chalcogen but easy with an excess of metals.

With this assumption we can understand why growth of the $CdGa_2Te_4$ layer is faster in metal-saturated reaction couples than with the Te-saturated samples (Fig. 8). By a small metal excess some of the interstitial vacancies of the ordered structure are filled with Cd or Ga, acting as defects for the metal interdiffusion (*2*), whereas, by Te saturation, these interstitial defects are destroyed (*3*):

$$\text{Me (g)} + V_i \rightarrow \text{Me}_i \qquad (2)$$

$$\tfrac{1}{2}\text{Te}_2\text{ (g)} + \text{Me}_i \rightarrow \text{Te}_{\text{Te}} + \text{Me}_{\text{Me}} + V_i \qquad (3)$$

(V_i = ordered vacancies in the chalcopyrite structure.)

As all structural vacancies in the disordered Ga_2Te_3-rich solid solutions act as normal defects in the metal sublattice, the defect formation portion of the activation energy of diffusion is omitted here. Therefore, the activation energy for cation interdiffusion in the Ga_2Te_3-rich region consists of only the migration part. This low activation energy explains, why at lower temperatures ($T < 900$ K), where long annealing times (~10 hr) are necessary, the Ga_2Te_3 crystal in the annealed reaction couples is nearly saturated with CdTe, whereas for higher temperatures with short annealing times (~1 hr) the saturation limit is not reached.

The vacancy flux in the Ga_2Te_3-rich solid solution, induced by the exchange of Ga with Cd, has the same direction as the Ga flux. It is retarded at the phase boundary of the $CdGa_2Te_4$ layer because of the much lower defect density in the metal sublattice of the ordered $CdGa_2Te_4$ phases as compared with the disordered Ga_2Te_3-phase. Thus, enrichment of vacancies at the phase boundary causes formation of pores which can aggregate in the groove, as shown in the micrographs (Figs. 5, 7). This effect is most pronounced at low temperatures, where the solubility of Ga_2Te_3 in the $CdGa_2Te_4$ phase is negligible. With increasing temperature the solubility increases and the vacancy density in the metal sublattice grows linearly with the Ga_2Te_3 excess (*4*):

$$Ga_2Te_3 \xrightarrow{CdGa_2Te_4} 2Ga_{Ga} + V_{Ga} + 3Te_{Te} \quad (4)$$

The higher this vancacy density the lower the retarding effect on the vacancy flux and the lower the tendency for formation of pores. Thus with increasing temperature the region for which the porosity is high enough to form a visible groove drifts from the phase boundary into the product layer. This mechanism explains the experimental observation that the groove drifts from the Ga_2Te_3-rich border to the CdTe-rich border of the product layer with rising temperature.

With further increase in temperature the degree of order in the $CdGa_2Te_4$ phase decreases, as indicated by the temperature dependence of the lattice constant ratio c/a. This process also contributes to an increase of defect density. Thus, it is not surprising that at the highest temperatures, where the reaction could still be investigated, no groove occurs within the $CdGa_2Te_4$ layer, but a small one is found in the CdTe-rich solid solution (Fig. 9).

In those cases where the reaction was started from $CdGa_2Te_4$ and Ga_2Te_3 no matter transport is needed within the $CdGa_2Te_4$ crystal. At 873 K the $CdGa_2Te_4$ lattice transforms into the defect zincblende lattice of the Ga_2Te_3 at the same rate at which CdTe dissolves in Ga_2Te_3. Here vacancies, transported to the phase boundary by the interdiffusion process, are required for the phase transformation; thus no formation of porous zones or grooves occurs.

On the CdTe-rich side of the $CdGa_2Te_4$ layer the solid solution crystallizes also in the defect zincblende lattice in which at equilibrium the vacancy density should be half the Ga density. Pores are formed preferentially in regions with high convex curvature of the Ga concentration profile. At low temperatures, therefore, pores are formed near the miscibility gap on the Ga_2Te_3-rich side; at higher temperatures (923 K), where the miscibility gap has disappeared, the porous zone is situated on the Ga_2Te_3-rich side of the steep slope of the Ga intensity in the X-ray profiles. At still higher temperatures the profiles flatten and the highest density of pores is then found in the region of the steepest part of the metal profiles near the pure CdTe.

The growth kinetics of the "$Cd_5Ga_2Te_8$" layer is complementary to that of the neighboring $CdGa_2Te_4$ layer. The former layer grows faster for Te-saturated than for metal saturated samples. In the "$Cd_5Ga_2Te_8$" layer about one-eighth of the sites of the metal sublattice are still vacant; saturation with tellurium does not significantly enhance the defect density of this region. The acceleration of growth of this layer by Te saturation must be induced by enhancement of the diffusivity in the neighboring Ga_2Te_3-poor solid solution. Here the density of structural vacancies is already so small that saturation with tellurium—as in pure CdTe—increases the density of metal vacancies perceptibly (*14*):

$$\tfrac{1}{2}Te_2\ (g) \xrightarrow{CdTe} Te_{Te} + V_{Cd}$$

At temperatures higher than 900 K the phase boundary within the zincblende lattice has disappeared, as the miscibility gap closes at about 890 K. For reactions above the critical temperature the solid solution affects the transport properties. In the composition region near the critical point the concentration profiles of Cd and Ga, as derived from the X-ray intensity profiles, run steeper than elsewhere in the solid solution. A maximum in the slope of a profile corresponds to a minimum in the diffusion coefficient. Quantitatively this behavior is expressed by the thermodynamic factor of the diffusion coefficient, which is zero at the critical point. With increasing temperature the solid solution becomes more nearly ideal, the cation profiles flatten more and more, and the thermodynamic factor approaches the value of 1.

Acknowledgments

Financial support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is acknowledged.

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