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Growth of $Cu_{1-x}Ga_xCr_2Se_4$ single crystals by chemical vapour transport and their electrical properties

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Abstract

Octahedral crystal up to 3 mm in length of $Cu_{1-x}Ga_xCr_2Se_4$ (x=0.1–0.9) were grown by the chemical transport method in a closed tube using CuSe, Ga_2Se_3 and $CrCl_3$. Electrical properties depend on chemical compositions. X-ray microanalysis and laser micro inductively coupled plasma spectrometry were used to verify the chemical composition.

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1. Introduction

Monocrystals of $Cu_{0.5}Ga_{0.5}Cr_2Se$ have been prepared using a chemical transport method and $CuCl_2$ as a transport agent [1]. The conditions of solid state reactions and the electrical and magnetic properties of prepared polycrystals of $Cu_{0.5}Ga_{0.5}Cr_2Se_4$ have been described in other papers [2–6]. Monocrystals of $Cu_{1-x}Ga_xCr_2Se_4$ with various compositions are not yet known.

The use of various conditions for the chemical vapour transport reaction [7–14] makes it possible to obtain spinels with a wide spectrum of gallium concentrations [15, 16].

It seems important to obtain $Cu_{1-x}Ga_xCr_2Se_4$ compounds and to investigate their chemical composition and electrical properties [15, 17].

2. Experimental procedure

2.1. Computation of equilibrium constants for the chemical transport reactions

Several chemical reactions may occur in the CuSe–Ga_2Se_3–$CrCl_3$ system. These reactions are very important in the chemical transport reaction and crystallization of spinels in various ways. The equilibrium constants were calculated as a function of $1/T$ to determine for example the transport ability of $CrCl_3$.

Experimental thermodynamic data from the literature were used in the calculations (ΔH°_{298} heat of formation; ΔS°_{298}, enthalpy; coefficients a, b and c in equation $C^\circ_p = a + b \times 10^{-3}T + c \times 10^5 T^2$; C_p, molar heat for the corresponding compounds; values in Table 1).

The transport agent $CrCl_3$ [19, 23] dissociates to $CrCl_2$, $CrCl_4$ and Cl_2 above 773 K. The partial pressures of Cl_2, $CrCl_2$ are very low compared with the partial pressures $CrCl_3$ and $CrCl_4$. The partial pressure coefficient Q is 20 at 830 K because during sublimation of $CrCl_3$ the gas phase contains 5% $CrCl_4$ [19] as well as $CrCl_3$. These transport reactions, during which $CrCl_3$, $CrCl_4$ and Cl_2 are transport agents, were used to calculate the equilibrium coefficients. It is possible to compute the equilibrium coefficients in heterogenous system (a gas phase and some solid phases) using the computer program EPCBN [24] or the newer EKVI SYSTEM [25].

For the CuSe–Ga_2Se_3–$CrCl_3$ system (Fig. 1) values of log K_a for transport reactions are similar to values of the state of equilibrium (log $K_a \approx 0$). $CrCl_4$ which appears in the ampoule ($T > 500$ K) could be a better transport agent because of its value of log K_a, which is close to zero (Fig. 2).

The transport ability of chlorine is disadvantageous for this system. The CuSe–Ga_2Se_3–$CrCl_3$ system fulfills conditions for the simultaneous transport of CuSe, Ga_2Se_3 (the same sign of enthalpy and the same value

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TABLE 1. Thermochemical data of the solid (s) and gaseous (g) states used for the computations of this work

Species	ΔH°_{298} (kJ mol^{-1})	S°_{298} (J mol^{-1} K^{-1})	a (J mol^{-1} K^{-1})	$b\times10^3$ (J mol^{-1} K^{-1})	$c\times10^{-5}$ (J mol^{-1} K^{-1})	Reference
CuSe(s)	−41.85	78.259	54.823	0	0	18
Ga_2Se_3(s)	−405.495	194.184	105.754	35.321	0	18
$CrCl_2$(g)	−142.290	278.302	60.142	2.218	−2.603	19
$CrCl_3$(g)	−331.452	316.804	87.278	−0.715	−12.940	19
$CrCl_4$(g)	−431.892	354.888	107.202	0.472	−10.554	19
GaCl(g)	−81.774	240.052	38.008^a	0^a	−2.012^a	18
$GaCl_2$(g)	−241.238	300.912	57.970^b	0.165^b	−4.733^b	20
$GaCl_3$(g)	−431.573	325.037	83.012^b	0.062^b	−7.983^b	20
Ga_2Cl_6(g)	−955.0	500.525	183.045^c	−0.158^c	−18.169^c	20
CuCl(g)	−91.107	237.151	37.284^a	0.539^a	−1.954^a	21
Cu_3Cl_3(g)	−258.633	429.506	132.794^a	0.138^a	−7.361^a	21
Se_2(g)	138.218	246.915	44.612	−2.657	−2.481	18
Cl_2(g)	0	223.114	36.921	0.251	−2.880	22

^{a}For 298–2000 K. ^{b}For 773–1773 K. ^{c}For 873–1773 K.

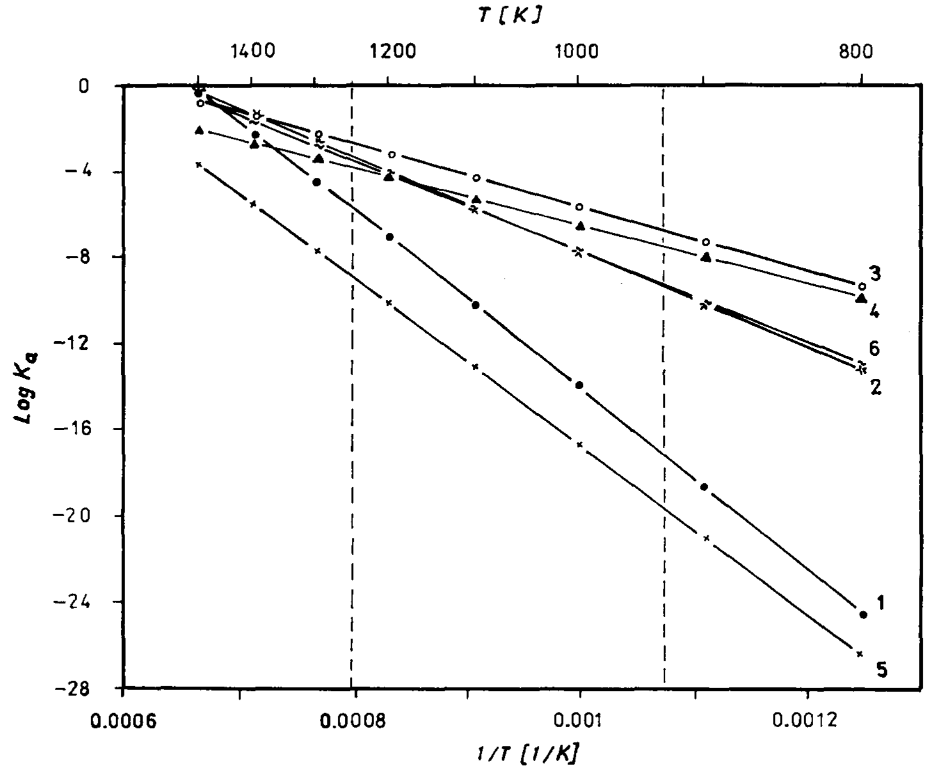

Fig. 1. The dependence of equilibrium constant K_a on $1/T$ for 1 (●) Ga_2Se_3, s + $2CrCl_3$, g $\rightleftharpoons$ 2GaCl, g + $2CrCl_2$, g + $\frac{3}{2}Se_2$, g; 2 (−) $\frac{1}{2}Ga_2Se_3$, s + $2CrCl_3$, g $\rightleftharpoons$ $GaCl_2$, g + $2CrCl_2$, g + $\frac{3}{4}Se_2$, g; 3 (○) $\frac{1}{3}Ga_2Se_3$, s + $2CrCl_3$, g $\rightleftharpoons$ $\frac{2}{3}GaCl_3$, g + $2CrCl_2$, g + $\frac{1}{2}Se_2$, g; 4 (▲) $\frac{1}{3}Ga_2Se_3$, s + $2CrCl_3$, g $\rightleftharpoons$ $\frac{1}{3}Ga_2Cl_6$, g + $2CrCl_2$, g + $\frac{1}{2}Se_2$, g; 5 (+) 2CuSe, s + $2CrCl_3$, g $\rightleftharpoons$ 2CuCl, g + $2CrCl_2$, g + Se_2, g and 6 (~) 2CuSe, s + $2CrCl_3$, g $\rightleftharpoons$ $\frac{2}{3}Cu_3Cl_3$, g + $2CrCl_3$, g + Se_2, g.

of the volatility) and crystallization of $Cu_{1-x}Ga_xCr_2Se_4$ spinel.

On the basis of reactions (1)–(12) (Figs. 1 and 2), we can expect [26–28, 30] the following gaseous species in the CuSe–Ga_2Se_3–$CrCl_3$ system: Cu_2Cl_4, Cu_4Cl_4, Cu_5Cl_5, $Ga_2Cl_4Cr_2Cl_4$. Selenium Se_x (x = 1–8) [29, 30] and mixed chlorides ($CuGa_2Cl_8$, $CuGaCl_5$) arising from melting metal chlorides by dissociation, association [31–34] and synthesis [35, 36] reactions could also be present.

2.2. Preparation of substrates and crystal growth

$Cu_{1-x}Ga_xCr_2Se_4$ monocrystals were obtained from elemental copper (purity 99.999%), gallium (purity 99.999%), selenium (purity 99.999%) and chromium chloride (purity 99.999%). Copper selenide (CuSe) and

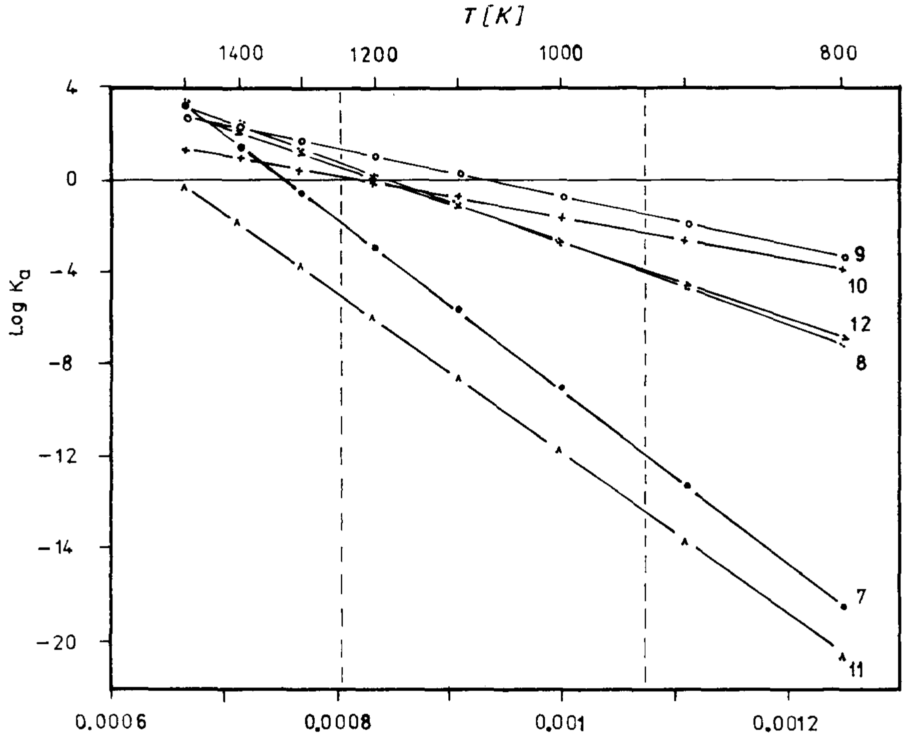

Fig. 2. The dependence of equilibrium constant K_a on 1/T for 7 (●) Ga_2Se_3, s + $CrCl_4$, g ⇌ 2GaCl, g + $CrCl_2$, g + $\frac{3}{2}Se_2$, g; 8 (··) $\frac{1}{2}Ga_2Se_3$, s + $CrCl_4$, g ⇌ $GaCl_2$, g + $CrCl_2$, g + $\frac{3}{4}Se_2$, g; 9 (○) $\frac{1}{3}Ga_2Se_3$, s + $CrCl_4$, g ⇌ $\frac{2}{3}GaCl_3$, g + $CrCl_2$, g + $\frac{1}{2}Se_2$, g; 10 (+) $\frac{1}{3}Ga_2Se_3$, s + $CrCl_4$, g ⇌ $\frac{1}{3}Ga_2Cl_6$, g + $CrCl_2$, g + $\frac{1}{2}Se_2$, g; 11 (∧) 2CuSe, s + $CrCl_4$, g ⇌ 2CuCl, g + $CrCl_2$, g + Se_2, g and 12 (>) 2CuSe, s + $CrCl_4$, g ⇌ $\frac{2}{3}Cu_3Cl_3$, g + $CrCl_2$, g + Se_2, g.

gallium selenide (Ga_2Se_3) were synthesized [37] in silicon ampoules evacuated to a pressure of about 10^{-5} Torr.

Phase analysis of metal selenides was realized by X-ray diffraction methods. The investigations on monocrystal growth in the CuSe–Ga_2Se_3–$CrCl_3$ system were performed for the following amounts of substrates: CuSe, from 1.6 to 14.4 mmol; Ga_2Se_3, from 0.1 to 5.18 mmol; $CrCl_3$, 6 and 8 mmol; the CuSe: Ga_2Se_3 was 0.3–130.

The transport agent $CrCl_3$ was prepared according to the method of ref. 38. Silicon ampoules of 20 mm inner diameter and 150–180 mm length containing powdered substrates were evacuated to about 10^{-5} Torr. A horizontal zone furnace with a melting zone temperature of 1053–1253 K and crystallization zone temperatures of 935–1101 K was used. The furnace was slowly cooled after six days of heating. Octahedral monocrystals of about 0.3–4 mm edge length were obtained.

2.3. *Chemical composition and the lattice parameters of monocrystals*

The chemical composition of $Cu_{1-x}Ga_xCr_2Se_4$ was determined by an X-ray microanalyser (JOEL 783). Copper (99.999%), gallium (99.999%) and chromium (99.999%) were used as standards; stoichiometric ZnSe was applied as a standard for selenium. The chemical composition was also determined by spectrophotometric analysis using laser micro (LM) inductively coupled plasma (ICP) optical emission spectroscopy (OES) [39].

2.3.1. *Analytical performance*

ICP spectrometry permits simultaneous multielement analysis by steady excitation conditions and with low matrix effects. An interesting expansion in the application of this technique is the possibility of direct solid sample analysis, if one takes into consideration the disadvantages of liquid analysis, such as degree of dilution, contamination from reagents, and the time delay necessary for sample pretreatment.

With the development of a number of so-called "tandem techniques" *e.g.* LM ICP spectrometry or LM ICP Mass spectrometry a wide variety of analytical problems can be solved.

L Micro ICP spectrometry represents a technique which, although not developed and used under these circumstances so far, has proved to be an injection technique. A focused short pulse laser is used to ablate a certain (microgram) amount from a solid sample in a sample chamber, and the vapour and droplets condense into small particles. After that, the aerosol is carried by flowing argon through a tube into an ICP for secondary excitations, and finally analysed by an atomic emission spectrometer [40–45]. Until now short-time sampling has not guaranteed the formation of a continuous signal in any known case, so that this technique bears a slight resemblance to flow injection analysis in its characteristics. The principle of the equipment which allows the introduction of both liquid and solid-generated aerosols is shown in Fig. 3. The carrier gas stream is split and fixed at the optimal height by variation of the nozzle section at the sample chamber. In order to optimize the transport processes several chamber designs have been evaluated. The chamber [46] used in this work is shown in Fig. 4.

LM analysis permits the qualitative and quantitative investigation of conducting and non-conducting materials. Results of both methods are presented in Tables 2 and 3.

The lattice parameters of $Cu_{1-x}Ga_xCr_2Se_4$ crystals were determined by the Bond method. The Bond method is a diffractometric method allowing the Bragg angle θ_{hkl} to be accurately determined for perfect single crystals, making use of a single reflection. This angle is found from the difference between the two positions of the single crystal which satisfy the Bragg condition in a very precise way. By eliminating the basic errors inherent in the traditional diffractometric method such as non-central position of the sample and the zero setting of the goniometric scale, this method enables a precision $\delta a/a$ greater than 10^{-6} to be achieved. To obtain a diffraction curve of half width 6′ at an angle 80° with an accuracy of 1″, systematic errors associated with refraction, vertical and horizontal divergence etc., which could cause displacement of the position of the reflection, must be eliminated by introducing suitable corrections.

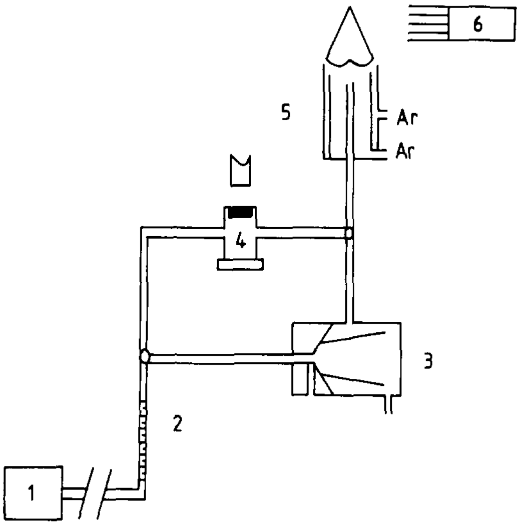

Fig. 3. Principle of experimental equipment. (1) Carrier gas, (2) rotameter, (3) nebulizer, (4) sample chamber, (5) ICP torch, (6) spectrometer.

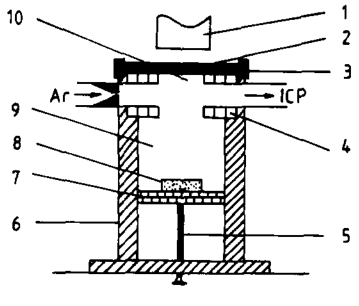

Fig. 4. Sample chamber for LM-ICP-OES. (1) Laser, (2) window, (3) screw cap, (4) adapter, (5) adjusting screw, (6) supporting base, (7) movable table, (8) sample, (9) sample space, (10) evaporation space.

TABLE 2. Chemical composition of $Cu_{1-x}Ga_xCr_2Se_4$ monocrystals determined using analysis performed on the X-ray microanalyser and analysis performed by laser micro inductively coupled plasma optical emission spectroscopy

Sample number	Concentrations of the following elements (wt.%)				Chemical formula
	Se	Cr	Cu	Ga	
X-ray microanalyser					
1	60.61	20.54	7.91	6.57	$Cu_{0.63}Ga_{0.48}Cr_2Se_{3.89}$
2	60.59	20.58	11.93	2.28	$Cu_{0.95}Ga_{0.165}Cr_2Se_{3.88}$
3	59.8	20.58	13.22	0.55	$Cu_{1.05}Ga_{0.04}Cr_2Se_{3.83}$
LM ICP OES					
1	63.53	22.55	7.4	6.52	$Cu_{0.537}Ga_{0.431}Cr_2Se_{3.71}$
2	58.23	25.21	13.61	2.95	$Cu_{0.884}Ga_{0.175}Cr_2Se_{3.041}$
3	53.55	29.51	16.41	0.53	$Cu_{0.91}Ga_{0.027}Cr_2Se_{3.39}$
Monocrystals obtained from one ampoule					
4	64.86	23.35	5.39	6.40	$Cu_{0.377}Ga_{0.409}Cr_2Se_{3.659}$
5	63.96	23.73	5.10	7.21	$Cu_{0.351}Ga_{0.453}Cr_2Se_{3.549}$
6	66.42	22.18	4.88	6.52	$Cu_{0.360}Ga_{0.438}Cr_2Se_{3.943}$
7	64.63	23.66	5.09	6.62	$Cu_{0.352}Ga_{0.417}Cr_2Se_{3.598}$
8	65.39	23.15	4.86	6.60	$Cu_{0.344}Ga_{0.425}Cr_2Se_{3.721}$

In our case measurements were performed for $Cu_{1-x}Ga_xCr_2Se_4$ single crystals grown by the chemical vapour transport method. For these measurements Cu Kα_1 radiation was used and the 12,4,4 reflection at angles of 75.1°–77.4°. These measured values depend on the compositions of the samples. The positions of reflections were observed numerically making use of the extrapolated "mid-chord" peak procedure. The relative error $\delta a/a$ of the measurement was 10^{-5}. Lattice parameter values are presented in Table 3. Values of the parameter a are given with account taken of refraction.

2.4. Measurements of electrical resistivity and Seebeck coefficient

Monocrystals obtained were characterized by two-probe d.c. resistivity measurement [15, 17] in the tem-

TABLE 3. Lattice parameter values of selected monocrystals of $Cu_{1-x}Ga_xCr_2Se_4$ samples with conditions of growth

Sample number	$n(CuSe)/n(Ga_2Se_3)$	ΔT^a (K)	$T_{c.z.}$ (K)	Lattice parameter details		Chemical formula
				a (pm)	$\delta a/a$	
1	1.85	105	965	1046.79	10^{-5}	$Cu_{0.48}Ga_{0.52}Cr_2Se_4$
2	1.19	83	970	1054.08	10^{-5}	$Cu_{0.2}Ga_{0.8}Cr_2Se_4$
3	0.70	169	1086	1054.09	10^{-5}	$Cu_{0.2}Ga_{0.8}Cr_2Se_4$
4	0.70	135	935	1055.22	10^{-5}	$Cu_{0.2}Ga_{0.8}Cr_2Se_4$
5	0.70	142	1099	1057.12	10^{-5}	$Cu_{0.1}Ga_{0.9}Cr_2Se_4$

$^a\Delta T = T_{m.z.} - T_{c.z.}$, $T_{m.z.}T_{c.z.}$ — temperature melting and crystallization zone.

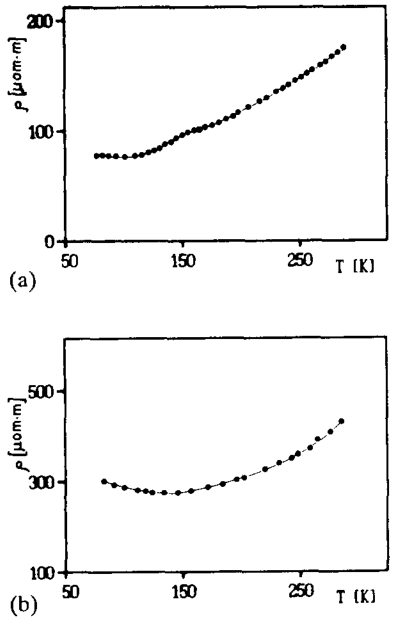

Fig. 5. Temperature dependence of the electrical resistivity for single crystal $Cu_{1-x}Ga_xCr_2Se_4$ where and (a) $x=0.1$ and (b) $x<0.8$.

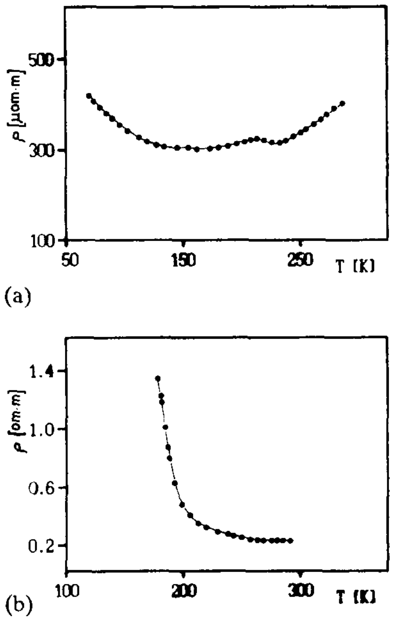

Fig. 6. Temperature dependence of the electrical resistivity for single crystal $Cu_{1-x}Ga_xCr_2Se_4$ where (a) $x>0.5$ and (b) $x=0.8$.

perature range 77–293 K with a stabilized current of 1 mA.

A voltameter (V-545) was used for measuring the voltage drop. Electrodes were made of the eutectic Ga–In alloy (83.5:16.5).

The measurements of the Seebeck coefficient [47] were carried out for selected monocrystals of $Cu_{1-x}Ga_xCr_2Se_4$ samples, where $0<x<0.5$, in the temperature range 295–354 K.

The automatic measuring device stabilized a constant temperature difference $\Delta T' = T_2 - T_1 = 5$ K across the sample, giving a constant average temperature $T_{av} = (T_1 + T_2)/2$.

The thermoelectric force was measured using a voltameter (V-545 type). The parallelepipedal samples for the measurements with thicknesses of 0.5–0.7 mm were cut from the octahedral monocrystals and placed between two copper blocks with copper–constantan thermocouples mounted on them. The accuracy of the temperature measurements was ±0.01 K and of the thermoelectric force ±10 μV.

The Seebeck coefficient was determined on the basis of the equation- $\alpha = SEM/(T_1 + T_2)$. The temperature dependence of the electrical resistivity and the Seebeck coefficient for monocrystals with various compositions are presented in Figs. 5–7.

3. Summary and conclusions

The use of $CrCl_3$ as a transport agent in the chemical vapour transport method, based on thermodynamical calculations, was found to be successful and is experimentally confirmed.

The change in lattice parameters up to 1057.12 pm (Table 3) is connected with the degree of copper substitution by gallium in $Cu_{1-x}Ga_xCr_2Se_4$ monocrystals. The maximum of the lattice parameter is connected

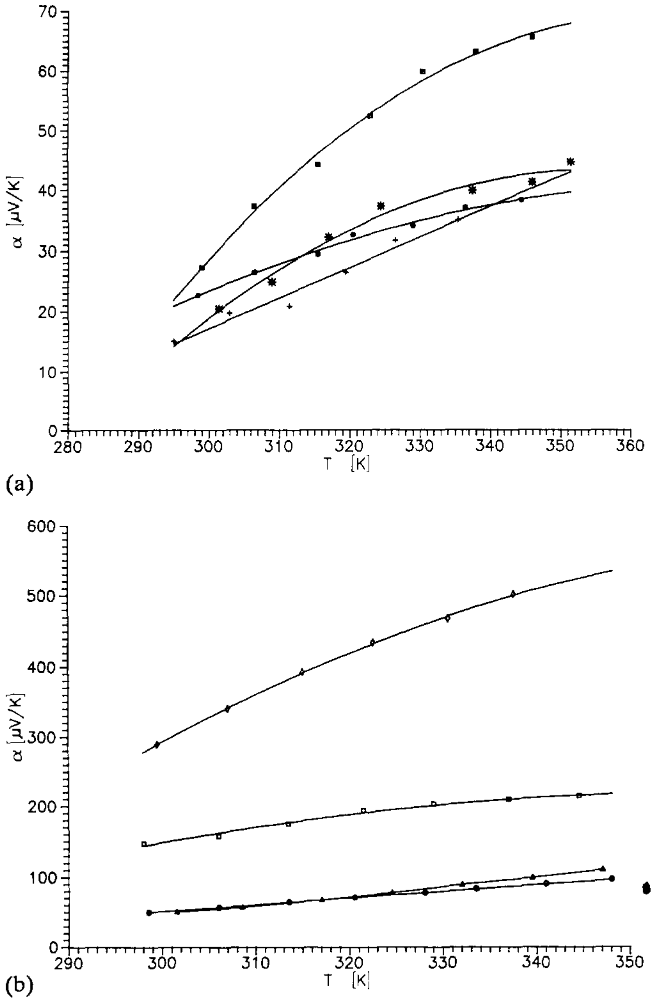

Fig. 7. Temperature dependence of the Seebeck coefficient for single crystals $Cu_{1-x}Ga_xCr_2Se_4$ where (a) $x<0.5$ and (b) $x>0.5$.

with a maximum gallium substitution in $Cu_{1-x}Ga_xCr_2Se_4$ spinel.

The temperature dependence of the electrical resistivity for $Cu_{1-x}Ga_xCr_2Se_4$ monocrystals changes with chemical composition (Figs. 5 and 6). Monocrystals with a lower gallium concentration (Fig. 5) exhibit a metallic type of resistance. The temperature dependence of the resistivity for this monocrystal is smaller at low temperatures than for $CuCr_2Se_4$ monocrystals [48].

Monocrystals with $x>0.5$ (Fig. 6(a)) display two mechanisms of conductivity, *i.e.* metallic from 200 K to 298 K and semiconducting from 78 K to about 200 K which explains the occurrence of a resistivity minimum. The electrical resistivity has a semiconducting type of temperature dependence for $x=0.8$ (Fig. 6(b)). The activation energy E_a calculated for this monocrystal is 0.396 eV.

The change in the character of the electrical resistivity from metallic in $CuCr_2Se_4$ to semiconducting in $Cu_{1-x}Ga_xCr_2Se_4$ could be connected with filled-in free sublevels in the basic band of copper and chromium.

Studies of the Seebeck coefficient show that the sign of the thermoelectrical force of the colder junction was positive for all samples. This indicates that crystals of the $Cu_{1-x}Ga_xCr_2Se_4$ series are characterized by hole conductivity (type p).

It 'was observed that, with the increase in x, the Seebeck coefficient increases (Fig. 7). This may be explained by the fact that monocrystals of $Cu_{1-x}Ga_xCr_2Se_4$ exhibit different electrical properties depending on x.

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