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TRANSITION METAL IONS AS STOICHIOMETRY SENSORS OF CuGaS$_2$ (*)

H. J. VON BARDELEBEN, A. GOLTZENE and C. SCHWAB

Laboratoire de Spectroscopic et d’Optique du Corps Solide,
L. A. 232 du C. N. R. S., Université Louis-Pasteur,
67084 Strasbourg Cédex, France

Abstract. — The overall stoichiometry compensation through transition ion valency changes has been studied in CuGaS$_2$. For this purpose, Ni and Fe were used as ionic sensors of the matrix state, as these impurities are already present in the as-grown material.

The valency changes could be observed either by electron spin resonance or Mossbauer absorption.

With increasing sulphur content, the valency of Fe increases first, followed by that of Ni. Further compensation is achieved by creation of intrinsic hole excess centres, associated with the copper vacancy.

The experimental results are discussed within the framework of a simple defect chemistry model of CuGaS$_2$.

1. Introduction. — During recent years, the band structure [1], the electrical [2, 3] and optical [4-6] properties of CuGaS$_2$, belonging to the I-III-VI$_2$ chalcopyrite family compounds have been investigated quite extensively.

Particularly, it could be shown that the most intense band edge recombinations were governed by the usual donor-acceptor process [4-6]. As a consequence, p type CuGaS$_2$ could be associated with n type CdS for devising green light emitting heterodiodes [7].

Several attempts were made in order to identify the nature of the defects involved in these spectra, the copper vacancy thus appearing as the most probable candidate for the acceptor level [2, 5].

On the other hand, if both optical and electrical properties were shown to depend strongly on stoichiometry alterations by sulphur annealings, the influence of transition metal contamination has only been recognized recently [8].

A similar situation has been encountered in the case of CuAlS$_2$, where only the simultaneous control of the valence state of the natural contaminants during doping lead to the desired electrical conductivity type [9].

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In most of our CuGaS$_2$ samples, Fe and Ni appear as major trace impurities. Therefore we are reporting here some results of our electron spin resonance (e. s. r.) and Mössbauer spectrometry investigations on crystals which have been purposely doped with Fe and Ni in association with stoichiometry changes induced by sulphur annealings. In addition, e. s. r. evidence of the paramagnetic centre associated with the copper vacancy is mentioned.

Finally, the experimental results are discussed within the framework of a simple defect chemistry model of CuGaS$_2$.

2. Experimental. — The samples were prepared by the chemical vapour transport technique with iodine as the transporting agent [5]. The dopants were merely added to the starting materials in the growth ampoule.

The dopant concentration was about $10^{19}$ atoms cm$^{-3}$ which is approximately $10^3$ times higher than the impurity content in samples which were not intentionally doped.

The annealing process was conducted by dipping the as-grown crystals directly in the liquid sulphur. Typical conditions were 700 °C for 24 hours. After quenching to room temperature, the samples were washed in boiling CS$_2$ in order to remove the sulphur from the surface.
The e. s. r. spectra were recorded with a Thomson-CSF THN252, 3 cm band spectrometer. All spectra were performed at 4.2 K.

Besides the typical transition ion spectra of Fe$^{3+}$, Ni$^+$ and Ni$^{3+}$, all annealed crystals displayed a further photosensitive isotropic e. s. r. signal, with a Landé g-factor

$$g = 2.024 \pm 0.002.$$ 

The e. s. r. spectra of Fe$^{3+}$ [10], Ni$^+$ [11, 12] and Ni$^{3+}$ [13] are already well known, but neither Fe$^+$, Fe$^{2+}$ nor Ni$^{2+}$ have ever been detected by e. s. r. techniques in chalcopyrite structures. The occurrence of Fe$^{2+}$, simultaneously present with trivalent iron, could only be demonstrated by Mössbauer spectrometry [8] in $^{57}$Fe doped crystals (Fig. 1).

The annealings showed that the valence states of Ni and Fe and the relative amounts in each valence state are stoichiometry dependent.

Figures 2a and 2b show the comparison of a Ni and Fe doped crystal before and after annealing. The initial ratio of the Ni$^+$ content over the Ni$^{3+}$ content has changed from 6 to 0.1, whereas the initial ratio of the Ni$^{3+}$ content over the Fe$^{3+}$ content has changed only from 10 to 2.

Simultaneously, an absolute increase, by a factor of 7 for the Fe$^{3+}$ concentration and by a factor of 2 for the Ni$^{3+}$ concentration to be compared with the decrease by a factor of 40 for the Ni$^+$ concentration, is observed.

This means that the total amount of nickel (Ni$^+$ and Ni$^{3+}$) apparently decreased, which indicates that part of the nickel changed in an e. s. r. undetectable state, probably into Ni$^{2+}$.

Figure 2c shows the effect of a low temperature illumination of a heavily doped sample, whereas figure 3 shows the same line in an undoped sample. The isotropic photosensitive line is ascribed to a copper vacancy complex $[\square S_u]^{2-}$, as described fully elsewhere [14].
3. Discussion. — The results will be discussed within the framework of a simple model, based on the application of two balance equations, the first concerning the number of available sites and the second ensuring the overall electrical neutrality.

If we assume a single phase compound, with no interstitial ions and the components keeping their usual valence (Cu+, Ga3+ and S2−), no departure from stoichiometry is possible.

In comparison with chalcopyrite CuFeS2 and related systems [15], it may well be assumed that similarly, CuGaS2 is based on a closed packed sulphur structure. Consequently, only cation vacancies are to be considered.

With neutral vacancies, the general formula may be written:

\[
\text{Cu}_a \square_b \text{Ga}_d \text{S}_2^2^-
\]

by application of the balance equations, it leads to the system:

\[
a + b + c = 2 \\
a + 3b = 4
\]

from which, one deduces \(a \leq b\) for \(c \geq 0\), meaning that a departure from stoichiometry is only possible with a copper deficit.

The electrical balance needs the presence of three vacant copper sites for each gallium atom, in excess.

The general compound formula is then rewritten:

\[
\text{Cu}^{+}_{1-3x} \square_{2x} \text{Ga}^{3+}_{1+x} \text{S}_2^2^-
\]

where the limiting cases correspond to CuGaS2 and Ga3S3.

It should be pointed out that 2 \(x\) represents the total number of vacant cation sites, and that no prediction can be made concerning the actual distribution of the vacancies among Cu and Ga sites, though the ordering energy is likely to favour the former.

The simple charged vacancy may also be considered. From the general formula:

\[
\text{Cu}^+_a \square \text{Ga}^{3+}_b \text{S}_2^2^-
\]

one may deduce the system

\[
a + b + d = 2 \\
a + 3b + d = 4
\]

leading to

\[
\text{Cu}^+_{1-y} \square \text{Ga}^{3+} \text{S}_2^2^-
\]

Contrary to the former situation, Cu vacancies may exist without the need for a Ga excess. Furthermore, if the positive charge is delocalized, it may be fixed by a S2− ion leading to a defect association \([\square \text{S}^-]^\cdot\). Such centres have already been observed in II-VI compounds, where the chalcogen anneal leads to the creation of the \(\Lambda\) centre [16].

It is believed that the hopping of a hole, arising from a copper vacancy, on the four nearest sulphur ions leads to a complex, denoted \([\square \text{S}_4]^\cdot\) with a consequent isotropic spectrum, in spite of the tetragonal deformation of the CuGaS2 lattice [17].

The easy creation of these vacancies might rest on the fact that Cu diffuses readily through the chalcopyrite lattice, creating a new copper sulphide layer at the surface and leaving empty copper sites in the bulk. This is supported by the usual low activation energy (0.5 eV) of the Cu diffusion in binary sulphides [18].

An actual intrinsic crystal would then correspond to the following formula in combining both types of vacancies:

\[
\text{Cu}^{+}_{1-3x-y} \square \text{Ga}^{3+}_{1+x} \text{S}_2^2^-
\]

Assuming that the annealing influences only the vacancy content, calling the increase of the sulphur content during the process \(\epsilon\) and denoting by \(\Delta\) the subsequent variations of the defect contents, we obtain:

\[
2 \Delta x + \Delta y = \epsilon \\
\Delta y = 2 \epsilon
\]

leading to \(\epsilon = -2 \Delta x\); the excess sulphur increase induces an equal decrease of the neutral vacancies.

Now, if transition metal impurities are incorporated into the lattice, additional compensation processes will be available through the possible valence changes.

The application of the former reasoning to a general case of a transition metal M, present in three valence states, involves too many parameters to allow any meaningful predictions without the help of ordering energy minimalization and chemical potential equations.

To restrict the number of parameters, the problem will be simplified by the consideration of the \(M^{2+}\) and \(M^{3+}\) states only.

A vacancy free crystal is described by the formula:

\[
\text{Cu}^+_a \text{M}^{2+}_b \text{M}^{3+}_d \text{Ga}^{3+}_b \text{S}_2^2^-
\]

from which it is immediately deduced that any alteration in composition necessitates vacancies, which is a situation similar to that of the pure compound.

Introduction of neutral vacancies leads to

\[
\text{Cu}^+_a \text{M}^{2+}_b \square \text{M}^{3+}_d \text{Ga}^{3+}_b \text{S}_2^2^-
\]

If we restrict our interest to the relative changes in composition of the defects, we obtain:

\[
\Delta x + \Delta \beta + \Delta y = \epsilon \\
2 \Delta x + 3 \Delta \beta = 2 \epsilon \\
\Delta x + \Delta \beta = 0
\]

This last equation is justified by the fact that the total impurity content remains constant during sulphurization.
The solution leads to the following relationships:
\[
e = - \frac{\Delta \alpha}{2} = \frac{\Delta \beta}{2} = \Delta \gamma.
\]
The decrease in the number of divalent ions is half as much as that of the increase in the sulphur excess, which is equal to the number of neutral vacancies created.

Consideration of the single ionized vacancy starts with the compound formula:
\[
\text{Cu}^+_2\text{M}^{2+}_3\square\overset{0}{\square}^\gamma\text{M}^+_3\text{Ga}^+_3\text{S}^-_2
\]
and ends with the system:
\[
\begin{align*}
\Delta \alpha + \Delta \beta + \Delta \delta &= \epsilon \\
2 \Delta \alpha + 3 \Delta \beta + \Delta \delta &= 2 \epsilon \\
\Delta \alpha &= \Delta \beta = 0
\end{align*}
\]
from which are derived
\[
\epsilon = - \Delta \alpha = \Delta \beta = \Delta \delta.
\]
For each S ion in excess, there is a change of one M$^{2+}$ ion into a M$^3+$ ion, whereas one single ionized vacancy is created.

Both situations may again be combined by the study of the interaction of the defect group:
\[
\text{M}^{2+}_2\square^\gamma\square^+\text{M}^+_3^2+
\]
The corresponding equations are:
\[
\begin{align*}
\Delta \alpha + \Delta \beta + \Delta \gamma + \Delta \delta &= \epsilon \\
2 \Delta \alpha + 3 \Delta \beta + \Delta \delta &= 2 \epsilon \\
\Delta \alpha &= \epsilon = 0
\end{align*}
\]
leading to
\[
\epsilon = - \Delta \alpha - \Delta \gamma = \Delta \beta - \Delta \gamma
\]
Although there is no longer an explicit proportionality between \( \epsilon \) and the content of some definite centres, the relations can be interpreted in the following manner.

Excess sulphur leads to vacancies; the total amount of both types is equal to the sulphur excess. It also induces a valence change of part of the M$^{2+}$ ions into M$^3+$ ions, partially compensated by an increase in the neutral copper vacancies.

It has been reported that CuFeS$_2$ accepts quite easily interstitial cations [15].

If we take account of the special mobility of copper, already mentioned in the previous section, only copper interstitial will be considered. Furthermore, as neither Cu$^0$ nor Cu$^{++}$ signals have been reported so far, only the Cu$^+$ interstitial will be dealt with.

As the M$^{2+}$ ions are known by e. s. r. measurements to exist only in one site, most probably the substitutional one, solely the M$^{2+}$ interstitials will be considered.

The active defects are therefore:
\[
\text{Cu}^+_2\text{Cu}^+_2\square\overset{0}{\square}^\gamma\text{M}^{2+}\text{M}^{3+}\text{M}^{2+}_3^3+
\]
The corresponding equations are:
\[
\begin{align*}
\Delta \alpha + \Delta \beta + \Delta \gamma + \Delta \delta + \Delta \varphi &= \epsilon \\
2 \Delta \alpha + 2 \Delta \alpha' + 3 \Delta \beta + \Delta \delta + \Delta \varphi + \Delta \varphi' &= 2 \epsilon \\
\Delta \alpha + \Delta \alpha' + \Delta \beta &= 0 \\
\Delta \varphi + \Delta \varphi' &= 0
\end{align*}
\]
from which one calculates:
\[
2 = \frac{1}{2} \left[ \Delta \delta - (\Delta \alpha' + \Delta \alpha) \right] = \frac{1}{2} (\Delta \delta + \Delta \beta).
\]
This shows that a sulphur excess yields an increasing charged vacancy concentration, partially compensated by the oxidation of M$^{2+}$ into M$^{3+}$.

Further relationships may be obtained; such as
\[
\epsilon = \Delta \varphi' + (\Delta \alpha' + \Delta \beta) = - \Delta \varphi + (\Delta \alpha + \Delta \beta)
\]
which means that excess sulphur induces Cu$^+$ to go into an interstitial position. This result, which is at first surprising, is to be related, to the fact that metal deficient CuGaS$_2$ must have copper vacancies if we do not consider interstitials as seen by setting \( \alpha = \alpha' = \beta = 0 \).

Although all these cases do not lead to unique solutions, they indicate a general trend towards a higher oxidation state of the transition metal ion. A similar observation can be made for the change of the neutral vacancy towards the charged one. The experimental data confirm the first assertion for both Ni and Fe.

Furthermore, it may be deduced from the experimental results, that the oxidation of the transition ions proceeds in stages. With increasing sulphur excess, we have first the Ni$^{1+}$ into Ni$^{2+}$ valence change, followed by the Fe$^{2+}$ into Fe$^{3+}$ transformation and finally by the Ni$^{2+}$ into Ni$^{3+}$ reaction. These oxidation processes are consistent with the oxidation potentials of the first row transition metals [19, 20].

Without illumination at low temperature, the charged copper vacancy is not observed.

These results show the possibility of distinguishing different phases in the oxidation states during the sulphurization process, which could lead to the use of transition metal ions as quantitative sensors of the stoichiometry of a crystal.

References