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Defect structure of $\text{Sb}_{2-x}\text{Cr}_x\text{Te}_3$ single crystals

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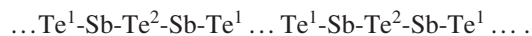
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Single crystals of Sb_2Te_3 doped with Cr ($c_{\text{Cr}}=0-6 \times 10^{20} \text{ cm}^{-3}$) were prepared by the Bridgman method. The measurements of the Hall coefficient reveal a nonmonotonous dependence of hole concentrations on the Cr content in the crystal. The hole concentration decreases at low content of Cr, while at higher content of Cr it increases again. However, according to magnetic measurements, Cr atoms enter the structure and form uncharged substitutional defects $\text{Cr}_{\text{Sb}}^{\times}$, which cannot affect the free carrier concentration directly. The observed dependence can be elucidated by means of a point defect model. The model is based on an assumption that defect structure of Sb_2Te_3 can be treated as hybrid Schottky and antisite defect disorder. Thus, we assume an interaction of $\text{Cr}_{\text{Sb}}^{\times}$ with the most populated native defects in the structure—antisite defects $\text{Sb}_{\text{Te}}^{-1}$ and vacancies in the Te sublattice $\text{V}_{\text{Te}}^{+2}$. © 2008 American Institute of Physics. [DOI: 10.1063/1.2826940]

I. INTRODUCTION

Antimony telluride Sb_2Te_3 crystals rank in the family of layered semiconductors with tetradymite structure (space group $D_{3d}^5-R\bar{3}m$). Their trigonal lattice is formed by a periodic arrangement of layers situated perpendicular to the trigonal c axis. Each layer is composed of five atomic planes arranged according to the following pattern:



Between the Te^1 atomic plane of neighboring atoms there is a van der Waals gap.¹ This compound is used as a component of materials for the construction of thermogenerators and solid-state coolers.² Therefore, an investigation of the effect of various dopants on the physical properties of Sb_2Te_3 is interesting both for basic and applied research.

In our previous paper³ we have shown that chromium doped Sb_2Te_3 is a new type of diluted magnetic semiconductor (DMS). Its Curie temperature T_C is proportional to the concentration of chromium and reaches the maximum value of 20 K for $x=0.095$. The content of chromium in this material and T_C were considerably enhanced up to $x=0.59$ and

190 K, respectively, using molecular beam epitaxy on sapphire substrates.⁴ Ferromagnetic behavior was also corroborated by the papers of Kulbachinskii *et al.*⁵⁻⁷

According to measurements of the Hall coefficient presented in Ref. 3, it is evident that low content of chromium in the structure of Sb_2Te_3 leads to a decrease of Hall concentration p down to a minimum at $x \approx 0.014$, while for higher concentration of chromium p increases again, reaching asymptotically the hole concentration of starting undoped Sb_2Te_3 . In this paper we aim to verify the anomaly of hole concentration and give a qualitative account of this within a model of point defects. The model is based on an interaction of uncharged substitutional defects $\text{Cr}_{\text{Sb}}^{\times}$ (chromium on the site of antimony) with native point defects occurring in the Sb_2Te_3 crystal lattice.

II. EXPERIMENTAL

The single crystals $\text{Sb}_{2-x}\text{Cr}_x\text{Te}_3$ were prepared from elements of 5 N purity using the modified Bridgman technique. The detailed description of crystal growth was published elsewhere.⁸ The Hall effect was measured using a Linear Research ac bridge with 16 Hz excitation in a magnet cryostat capable of fields up to 5 T.

The concentration of free current carriers p was obtained from the expression for the Hall constant $R_H(\mathbf{B} \parallel \mathbf{c}) = \gamma(r_H/pe)$, where e is the electron charge, γ is the structure factor, and r_H is the scattering factor. For γ we used the value

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TABLE I. The Hall concentration of holes p , the increment of hole concentration Δp , and concentrations of point defects as a function of chromium concentration c_{Cr} in $\text{Sb}_{2-x}\text{Cr}_x\text{Te}_3$ single crystals.

Sample No.	c_{Cr} $\times 10^{19}$ cm^{-3}	p $\times 10^{19}$ cm^{-3}	$^a[\Delta p]$ $\times 10^{19}$ cm^{-3}	$^1\text{Cr}_{\text{Sb}}^\times$ $\times 10^{19}$ cm^{-3}	$^2\text{Cr}_{\text{Sb}}^\times$ $\times 10^{19}$ cm^{-3}	$[\text{Sb}_{\text{Te}}^{-1}]$ $\times 10^{19}$ cm^{-3}	$[\text{V}_{\text{Sb}}^{-3}]$ $\times 10^{19}$ cm^{-3}	$[\text{V}_{\text{Te}}^{+2}]$ $\times 10^{19}$ cm^{-3}	$[\text{Sb}_{\text{Sb}}]$ $\times 10^{19}$ cm^{-3}	$^2\text{Cr}_{\text{Sb}}^\times/c_{\text{Cr}}$
1	0	7.46	0	0	0	11.84	11.84	19.95	9.36	
2	5.4	5.78	1.68	5.12	0.280	11.56	11.56	20.23	9.64	0.0519
3	6.5	6.42	1.04	6.33	0.173	11.67	11.67	20.12	9.53	0.0266
4	7.2	6.90	0.56	7.11	0.093	11.75	11.75	20.04	9.45	0.0129
5	8.5	5.08	2.38	8.10	0.397	11.44	11.44	20.35	9.76	0.0467
6	19.5	5.32	2.14	19.14	0.357	11.48	11.48	20.31	9.72	0.0183
7	29.0	6.08	1.38	28.77	0.230	11.61	11.61	20.18	9.59	0.0079
8	44.0	6.80	0.66	43.89	0.110	11.73	11.73	20.06	9.47	0.0025
9	60.0	6.90	0.56	59.99	0.093	11.75	11.75	20.04	9.45	0.0016

$$^a\Delta p = p(\text{Sb}_2\text{Te}_3) - p(\text{Sb}_{2-x}\text{Cr}_x\text{Te}_3).$$

of 0.74 given in Ref. 9 and we assumed that the value of γ does not change with the incorporation of Cr into the crystal lattice of Sb_2Te_3 . Moreover, we took the value of the scattering factor r_{H} to be unity, i.e., $r_{\text{H}}=1$. The approximate values of p , obtained in this way, are given in Table I.

Note: We are aware that the free carrier concentrations presented in Table I are approximate ones due to the occurrence of two types of holes characterizing the transport properties of Sb_2Te_3 . An estimate based on the parameters presented for Sb_2Te_3 in Ref. 10 yields a contribution of heavy holes to R_{H} of about 4%. We argue, however, that the chromium doping has negligible influence on band structure and thus cannot account for doping anomaly. We do not attempt to describe this interaction quantitatively. The numbers summarized in Table I should be considered as a rough approximation that expresses the tendency.

III. RESULTS AND DISCUSSION

As mentioned above, $\text{Sb}_{2-x}\text{Cr}_x\text{Te}_3$ crystals show ferromagnetic behavior, the maximum $T_{\text{C}} \approx 20$ K for the highest content of chromium $x=0.095$. The interpretation of the paramagnetic region within Curie-Weiss law^{3,7} gives the effective magnetic moment close to $3.8\mu_{\text{B}}$, showing that Cr atoms are present in the valence state +3. With regard to this magnetic moment and the crystal structure, we assume that Cr is octahedrally coordinated with Te atoms. Basically, Cr atoms can enter two positions in the Sb_2Te_3 crystal lattice. The first one is situated in the plane of Sb atoms (between the planes of Te^1 and Te^2), while the second one is in the middle of the empty octahedron inside the van der Waals gap with the apices formed by the Te^1 atoms of the adjacent Te^1 planes. The second location—the one placing Cr atoms in the van der Waals gap—is however very unlikely because such Cr ions would generate free electrons, leading to a decrease in the concentration of holes. Though we observe a decrease of hole concentration at low content of Cr, the hole concentration rises again at higher content of chromium, reaching asymptotically the value of starting pure Sb_2Te_3 (see Fig. 1). Also, the excellent cleavage characteristics of the crystals along a - b planes would be adversely affected by the presence of Cr atoms in the van der Waals gap. Thus we suppose that chromium substitutes for Sb and forms uncharged point

defects $\text{Cr}_{\text{Sb}}^\times$. This type of defect cannot account for the observed minimum (Fig. 1, Table I) in the dependence $p = f(c_{\text{Cr}})$ since it produces no free carriers. Thus, in contradiction with the assumption of uncharged point defect $\text{Cr}_{\text{Sb}}^\times$, we observe a nonzero doping efficiency and the ratio $\Delta p/c_{\text{Cr}}$ varies within the studied range from 0.34 to 0.012 (see Table I). As we show below, this discrepancy can be explained provided Cr atoms interact with native defects in the Sb_2Te_3 crystal lattice.

Native defects arise during crystal growth from melt and their concentration in Sb_2Te_3 is the consequence of the overstoichiometric content of antimony. The excess of Sb in the otherwise stoichiometrically weighed composition ($2\text{Sb} + 3\text{Te}$) is associated with a shift of the maximum of the solidus curve in the Sb-Te phase diagram toward the side of Sb.¹¹ Crystals of Sb_2Te_3 prepared from stoichiometric melts inevitably contain the following defects:

- vacancies in the Te sublattice that carry two positive charges, $\text{V}_{\text{Te}}^{+2}$,
- antisite defects (AS defects) such as Sb atoms on the Te sublattice that carry one negative charge, $\text{Sb}_{\text{Te}}^{-1}$,
- vacancies on the Sb sublattice with three negative charges, $\text{V}_{\text{Sb}}^{-3}$, and

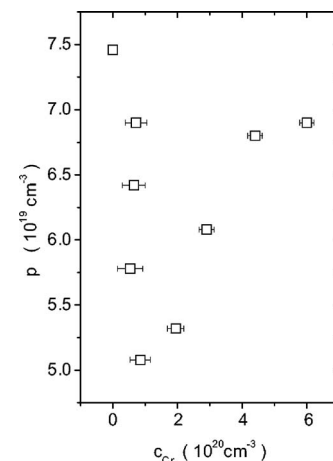
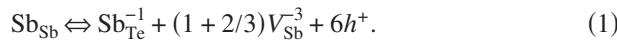


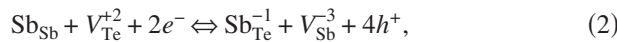
FIG. 1. The hole concentration p (from the measurement of the Hall coefficient) as a function of concentration of Cr in $\text{Sb}_{2-x}\text{Cr}_x\text{Te}_3$ single crystals. The error bars show the accuracy of determination of chromium concentration.

- (d) structural defects such as $\text{Sb}_3\text{Te}_4^{-1}$ and $\text{Sb}_4\text{Te}_5^{-2}$ (seven- and nine-layer lamellas observed in Ref. 12) that mimic the charge contribution of one, respectively two, antisite defects $\text{Sb}_{\text{Te}}^{-1}$.

To calculate the concentration of antisite defects $\text{Sb}_{\text{Te}}^{-1}$ and vacancies V_{Sb}^{-3} and V_{Te}^{+2} we use a model based on the idea that a certain part of the total overstoichiometric antimony, Sb_{over} , forms the antimony sublattice (denoted Sb_{Sb}) and the remaining part enters the Te sublattice forming antisite defects $\text{Sb}'_{\text{Te}2}$ (that means that the antisite defects are located on Te^2 atomic planes). Considerable understoichiometry of Te (as the chemical analysis shows) gives rise also to tellurium vacancies V_{Te}^{+2} . Since it is not possible to determine from the transport measurements if V_{Te}^{+2} vacancies are created in the Te^1 or Te^2 atomic planes we have assumed that the vacancies V_{Te}^{+2} compensating the negative charge of $\text{Sb}_{\text{Te}}^{-1}$ are concentrated in the Te^1 -planes. According to the model, the ratio of cation to anion sites is equal to 2:3. The model based on occurrence of AS defects and cation and anion vacancies can be understood as hybrid Schottky and antisite disorder,¹³ which is described by following equation:



To express explicitly the fact that the suppression of concentration of AS defects leads to formation of tellurium vacancies V_{Te}^{+2} , we can rewrite Eq. (1) using the equation $2V_{\text{Sb}}^{-3} + 3V_{\text{Te}}^{+2} = 0$ into the following form:



which describes the equilibrium of native defects. The equation allows us to formulate the changes of free carrier concentration induced, for instance, by the shift of content of overstoichiometric Sb or by an incorporation of foreign atoms. The equation also shows that formation of one AS defect is linked to formation of antimony vacancy V_{Sb}^{-3} .

We used this model with the help of chemical analysis of undoped crystal and measurement of hole concentration for the calculation of point defect concentration in undoped Sb_2Te_3 in our previous paper.¹⁴ The model bases on four equations:

$$[\text{Sb}_{\text{over}}] = [\text{Sb}_{\text{Sb}}] + [\text{Sb}_{\text{Te}}^{-1}], \quad (3a)$$

$$[\text{Sb}_{\text{Te}}^{-1}] = [V_{\text{Sb}}^{-3}], \quad (3b)$$

$$2[V_{\text{Te}}^{+2}] + [h^+] = [\text{Sb}_{\text{Te}}^{-1}] + 3[V_{\text{Sb}}^{-3}], \quad (3c)$$

$$([\text{Sb}_{\text{Sb}}] + [V_{\text{Sb}}^{-3}]) / ([V_{\text{Te}}^{+2}] + [\text{Sb}_{\text{Te}}^{-1}]) = 2/3. \quad (3d)$$

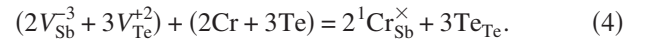
For a given composition of the single crystal $\text{Sb}_2\text{Te}_{2.95}$, the excess antimony amounts to $\text{Sb}_{\text{over}} = 21.2 \times 10^{19}$ Sb atom cm^{-3} . Together with the measured hole concentration of $p = 7.46 \times 10^{19}$ cm^{-3} we found following results: $[\text{Sb}_{\text{Sb}}] = 9.4 \times 10^{19}$ cm^{-3} , $[\text{Sb}_{\text{Te}}^{-1}] = 11.8 \times 10^{19}$ cm^{-3} , $[V_{\text{Sb}}^{-3}] = 11.8 \times 10^{19}$ cm^{-3} , and $[V_{\text{Te}}^{+2}] = 19.9 \times 10^{19}$ cm^{-3} . The results are in accordance with Eq. (2). Using the equation $2V_{\text{Sb}}^{-3} + 3V_{\text{Te}}^{+2} = 0$ we found the concentration of active tellurium vacancies, i.e., part of vacancies producing electrons: $[V_{\text{Te}}^{+2}] = 2.17 \times 10^{19}$ cm^{-3} .

The knowledge of the nature and concentration of the native defects allow us to clarify the discordance—an extreme in $p=f(c_{\text{Cr}})$ dependence. The starting conditions are as follows:

- Cr atoms do not enter the Te sublattice.
- Cr atoms neither form interstitials nor enter van der Waals gap.
- Cr atoms form formal +3 state exclusively.

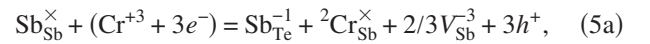
There are two ways of incorporation of Cr in the Sb sublattice.

(a) A certain part of the chromium in the form of Cr_2Te_3 enters the lattice and forms substitutional point defect $\text{Cr}_{\text{Sb}}^{\times}$ according to equation

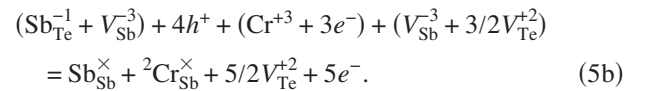


Chromium incorporated in this way, further denoted $^1\text{Cr}_{\text{Sb}}^{\times}$, liberates no free carriers.

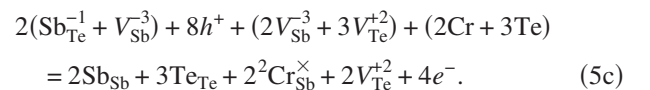
(b) The remaining part of the chromium atoms forming defects, denoted $^2\text{Cr}_{\text{Sb}}^{\times}$, interacts with the AS defects and the vacancies V_{Sb}^{-3} and V_{Te}^{+2} . The interaction must obey the equilibrium of Eq. (1) and it results in a change of hole concentration according to the following equation:



which describes formation of $^2\text{Cr}_{\text{Sb}}^{\times}$ defect and a decrease of hole concentration [compare with Eq. (1)]. Taking into account the occurrence of tellurium vacancies, Eq. (5a) converts to

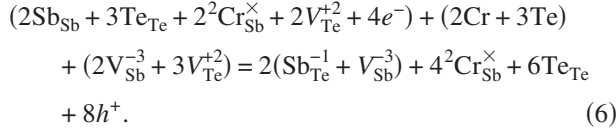


Equation (5b) expresses the idea that a Cr^{+3} ion occupies antimony vacancy V_{Sb}^{-3} , forming $^2\text{Cr}_{\text{Sb}}^{\times}$. This shifts the equilibrium of Eq. (2) in favor of tellurium vacancies V_{Te}^{+2} and produces six electrons per chromium atom. In the case of the experiment, Eq. (5b) must be modified since chromium is added as a stoichiometric mixture with tellurium ($2\text{Cr} + 3\text{Te}$):

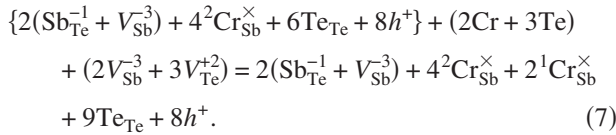


The interaction thus leads to disappearance of $\text{Sb}_{\text{Te}}^{-1}$ and V_{Sb}^{-3} , i.e., the equilibrium described by Eq. (2) shifts toward formation of V_{Te}^{+2} and electrons. This process runs to the point where the charge produced by the V_{Te}^{+2} is equal to the charge produced by both $\text{Sb}_{\text{Te}}^{-1}$ and V_{Sb}^{-3} . Once the charge produced by the defects is equal on both sides of Eq. (5c), i.e., $\text{Sb}_{\text{Te}}^{-1} + 3V_{\text{Sb}}^{-3} = 2V_{\text{Te}}^{+2}$, the incorporation of chromium cannot induce a further increase of the free electron concentration. The hole concentration as a function of concentration of chromium (Fig. 1) shows a minimum in the vicinity of $c_{\text{Cr}} = 0.9 \times 10^{20}$ cm^{-3} . Thus this minimum should correspond to equality $[\text{Sb}_{\text{Te}}^{-1}] + 3[V_{\text{Sb}}^{-3}] = 2[V_{\text{Te}}^{+2}]$. Although the contribution of negatively charged defects to concentration of free carriers ($\text{Sb}_{\text{Te}}^{-1} + 3V_{\text{Sb}}^{-3}$) was suppressed, the contribution of positively charged defects ($2V_{\text{Te}}^{+2}$) only approaches the contribution of the preceding ones (see Table I).

The increase of hole concentration from the minimum toward the higher concentration of chromium is linked to a shift of equilibrium (2) to the right. It can be expressed by the following equation:



It follows from Eq. (6) that one incorporated chromium atom in the form of $(2\text{Cr}+3\text{Te})$ liberates six holes and simultaneously increases the concentration of $(\text{Sb}_{\text{Te}}^{-1} + V_{\text{Sb}}^{-3})$ and suppresses the concentration of V_{Te}^{+2} and electrons. The process runs until the active tellurium vacancies are depleted. What is then left are the tellurium vacancies charge, which is compensated by V_{Sb}^{-3} . Under these circumstances the subsequent increase of chromium concentration has no influence on the concentration of the charged defects and hole concentration as expressed by the following equation:



According to Eq. (7) it is evident that from this point the chromium atoms entering the structure form $^1\text{Cr}_{\text{Sb}}^{\times}$ defects only and produce no free carriers. This would apply also for the case of any solubility. This result coincides with the experiment. Figure 1 indicates that for any studied concentration of chromium the concentration of holes remains under the starting value of undoped Sb_2Te_3 . This approach allows one to figure out the concentrations of the discussed defects as a function of chromium concentration. This calculation requires, in addition to Eqs. (2), (3a)–(3d), (4), (5a)–(5c), (6), and (7), the knowledge of the concentration of native defects in undoped Sb_2Te_3 and the hole concentration as a function of chromium content.

Equations (4), (5a)–(5c), (6), and (7) can be summarized as follows:

- The part of the chromium atoms forming the $^1\text{Cr}_{\text{Sb}}^{\times}$ defects produces no free carriers.
- The part of the chromium atoms forming the $^2\text{Cr}_{\text{Sb}}^{\times}$ defects suppresses the concentration of free carriers by six holes per one defect for the range of descending hole concentration.
- The part of the chromium atoms forming the $^2\text{Cr}_{\text{Sb}}^{\times}$ defects produces six holes per one defect for a range of rising concentration of holes (due to depletion of active tellurium vacancies).

It also applies that $[^1\text{Cr}_{\text{Sb}}^{\times}] + [^2\text{Cr}_{\text{Sb}}^{\times}] = c_{\text{Cr}}$. The results are figured out in Table I. We see that the ratio $[^2\text{Cr}_{\text{Sb}}^{\times}]/c_{\text{Cr}}$ is small and decreases (except for sample 5) with increasing concentration of chromium c_{Cr} (Fig. 2, Table I). This documents that only a small fraction of the chromium atoms interacts with the native defects while the majority forms $^1\text{Cr}_{\text{Sb}}^{\times}$ defects according to Eq. (4). In Fig. 3 we show the concentration of $\text{Sb}_{\text{Te}}^{-1}$ and V_{Te}^{+2} as a function of the $^2\text{Cr}_{\text{Sb}}^{\times}$ concentration, which documents the changes in Sb_2Te_3 due to chromium doping.

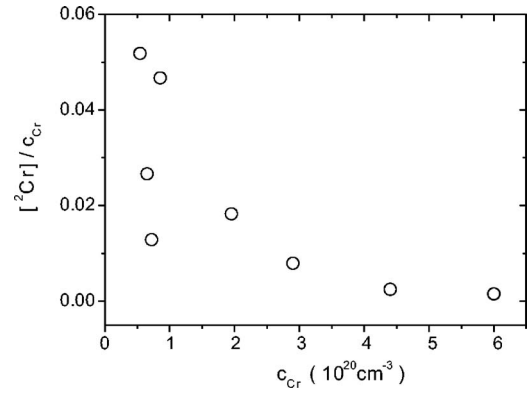


FIG. 2. The ratio $[^2\text{Cr}_{\text{Sb}}^{\times}]/[c_{\text{Cr}}]$ as a function of c_{Cr} in $\text{Sb}_{2-x}\text{Cr}_x\text{Te}_3$ single crystals.

Note that the way of incorporating chromium according to Eqs. (4) and (5a)–(5c) is different, however both ways produce the same point defects $\text{Cr}_{\text{Sb}}^{\times}$.

IV. CONCLUSIONS

- Single crystals of $\text{Sb}_{2-x}\text{Cr}_x\text{Te}_3$ ($c_{\text{Cr}}=0-6 \times 10^{20} \text{ cm}^{-3}$) were characterized by the measurement of electrical conductivity and the Hall coefficient at room temperature.
- The measurements reveal that the hole concentration as a function of chromium concentration shows an anomaly. The hole concentration first decreases and, after passing a minimum, it increases and approaches the hole concentration of pure Sb_2Te_3 .
- The anomalous dependence was analyzed within the hybrid Schottky and antisite defect disorder model. The model elucidates the defect structure. It provides approximate concentrations of cation and anion vacancies, antisite defects, and overstoichiometric antimony as a function of chromium concentration.
- The anomalous dependence, i.e., the occurrence of a minimum in $p=f(c_{\text{Cr}})$, is ascribed to the interaction of chromium with native defects. The interaction shifts the equilibrium reaction $\text{Sb}_{\text{Sb}} + V_{\text{Te}}^{+2} + 2e^{-} \leftrightarrow \text{Sb}_{\text{Te}}^{-1} + V_{\text{Sb}}^{-3} + 4h^{+}$ to the left for low concentration of chromium and, after reaching a minimum of hole concentration, shifts the reaction to the right.

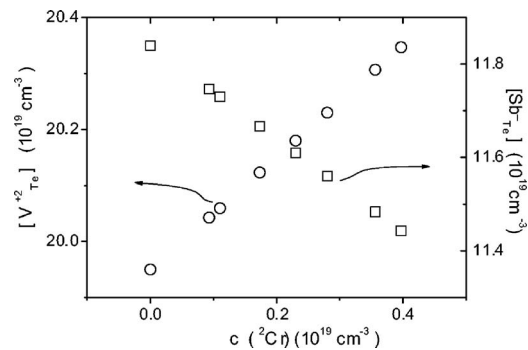


FIG. 3. The concentration of tellurium vacancies V_{Te}^{+2} and antisite defects $\text{Sb}_{\text{Te}}^{-1}$ as a function of concentration of $^2\text{Cr}_{\text{Sb}}^{\times}$ in $\text{Sb}_{2-x}\text{Cr}_x\text{Te}_3$ single crystals.

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