Origins of the p **-type nature and cation deficiency in Cu₂O and related materials**

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 $\begin{array}{cccccccccccccc} t & f & t & t & t & t & t & t & f t \\ & & & & t & t & t & t & f t & f t \\ & & & & & t & t & t & f & f t & \end{array}$ ing ZnO and In2 are naturally anion-deficient and electron conductors. Even fewer of the oxides are naturally cation-deficient and hole conductors, the arch-type of which is Cu2O. Based on first principles calculation ¹⁰- oxide-based materials are of equilibrium nonstoichiometry and defect stability, we explain why the Cu both -type and naturally cation-deficient, and why cation vacancies lead to delocalized, conductive states, \mathbf{t} in (\ldots, \ldots) , \mathbf{t} , they lead to localize states t

 $10.110 / 10.76$ 10.20 $()$ 1. $, -1$, 1.20 $, -1$, 2.20., 2.9.

I. INTRODUCTION

 \mathbf{t} t crystalline wide gap oxides are both stormal \mathbf{t} t crystalline \mathbf{t} and electrically insulating insulation in \mathbf{f} turally and the conductor[s](#page-4-2) $t = \frac{t}{2} + \frac{t}{E_g} + \frac{t}{2} + \frac{t}{E_g}$. $\frac{2}{t}$ b E_g . \cdot . smaller group are naturally cation-definition-definition-definition-definition-definition-definition-definitionto architecture of the latter is cuprimeter is cuprimeter is cuprimeter is cuprimeter is cuprite E_g 2.1), , and the group includes relation $t = \frac{10}{100}$ materials [s](#page-4-5)uch as $\frac{1}{2}$ denotes the such $\frac{1}{2}$ delay $\frac{1}{2}$ denotes $\frac{1}{2}$ [,](#page-4-4) $\begin{array}{ccc} \text{A} & \text{B} & \text{C} \end{array}$ $\begin{array}{ccc} \text{A} & \text{B} & \text{C} \end{array}$ $\begin{array}{ccc} \text{A} & \text{B} & \text{C} \end{array}$ and $\begin{array}{ccc} \text{A} & \text{B} & \text{C} \end{array}$ *X*_p). Such $-t$ are interested are interested as t and t ing as some of the are transparent with t , and combined with t k -type transparent conductive original conductive original k \mathbf{f} transparent electronics. Standard structural indicates in \mathbf{f} that is structural indicates in \mathbf{f} in \mathbf{f} is structural indicates in \mathbf{f} in \mathbf{f} is structural in \mathbf{f} in \mathbf{f} is str $t²$ explains in broad terms that an oxide will not $t²$ \mathbf{t} f \mathbf{t} its cation-definition-definition-definition-definition is oxidizable, i.e., \mathbf{t} more positive original number. Indeed, the existence of \mathbf{t} $\mathbf f$ and $\mathbf f$ and $\mathbf f$ and $\mathbf f$ and $\mathbf f$ the number of the theory of th metal cation indicates the propensity of the oxide to exist in a more cation-definition-definition-definition-definition-definition t and $(1, 0, 0, \frac{1}{2})$ $\left(\right)$ $\left(\begin{array}{c} \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \end{array} \right)$ $t \rightarrow$, we are a set $t \rightarrow t$ $\left(\right)$ how such conditions are accommodated microscopic microscopic microscopic microscopic microscopic microscopic m \mathbf{t} the cation definition definition definition definition \mathbf{t} cies, and \mathbf{t} is the correct interstitution in the correct or or oxygen and or oxygen and \mathbf{t}

what is the solubility limit of such defects in the host crystal, i.e., maximum concentration before the \mathbf{t} \mathbf{t} of \mathbf{t} \mathbf{t} fields \mathbf{t} $\left(\quad \right)$ how the cation definition definition definition t is t in t in t is $$ tity free holes. Based on first principles calculation of f equilibrium nonstoichiometry and defect t , we adjust t dere these for f_{1} in f_{2} . We find that in $\frac{1}{2}$, $() t$) the cation definition definition definition t $\begin{array}{c} \n\begin{array}{c}\n\overrightarrow{t}\n\end{array} \\
\end{array}$ t tt

f $\frac{1}{\sqrt{2}}$ $\frac{1}{\sqrt{2}}$ $\frac{10^{20}}{2}$, () t t concentration of *V*_Cu can reach 10² $()$ the *V*_Cu induces a host-derived acceptor level natural maker level naturally maker acceptor level naturally maker and induces a host-derived acceptor level in the contract of the contract of the contract of the contract ing $\frac{1}{2}$ -type, it that the concentration of the concentration of $\frac{1}{2}$ in $\frac{1}{2}$ temperature only reaches 10¹ cm−3 as not all \rightarrow \sim 10¹ ized to produce holes. Finally, we provide general design \mathcal{E} $r = f - t$

th[e](#page-4-7) discovery of $f-t$ and $\left(\begin{array}{ccc} 1 & 0 \\ 0 & -t \end{array}\right)$ (-10) , it was speculate[d](#page-4-4) to the compound term in t from the introduction of the introduction of covalence \mathbf{r} introduction of covalence intervalence of covalence intervalence in the other- \mathbf{t} ionic metal-oxide network, thus avoiding localization of \mathbf{t} the negatively charged oxygen ions. However, t

ever, the special feature of t -type of t -type of t -type of t functional orientation is the existence of a stabilism t of a stabilism of a stabili large concentration of holes; while introduction of covalency broadens the band and may lead to *lighter* effective may be may lead to *lighter* effective may be made to *lighter* \mathbf{f} and hence better carrier mobility, the *deable* the creation of holes in the first place. Indeed, equilib r in a substa[nt](#page-4-8)ial concentration of \mathbf{r} in a pure \mathbf{r} in a pure \mathbf{r} t control \mathbf{r} ()) ft point ft $\begin{array}{cccccccccccccc} f & t & t & t & f & e & e \\ \end{array}$, e.g., e.g., t t t \mathbf{u} ()) by the small interval in \mathbf{f} the small interval in \mathbf{f} ft to to readily release holes in the shallow acceptor \mathfrak{t} . $\begin{array}{cccccccccccccc} t & t & t & t & t & \cdots & t & \cdots & t & \cdots & \cdots \end{array}$ \mathbf{t} and \mathbf{t} $\left(\quad \right)$ f t formation energy of f *hole killers* e.g., native donors such as cation interstitials and animal vacancies $\left(\begin{array}{cc} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 &$). $t t$ that t the latter condition is the latter condition is t $r = f \cdot tt \quad t \quad t \quad t$ erate international or t introduction of t the creation of structural hole killers. Additional hole killers. Additionally, for a *g*ood $-t$ ^t $e \sim t$

, facilitating a low effective hole mass and $\mathbf f$ thus high mobility. Here, we show that in t (10) $\frac{t}{f}$, () t $\frac{1}{\sqrt{2}}$ \mathbf{t} both in the cuprite structure \mathbf{t} $\mathbf{t} \left(\mathbf{t} \mathbf{t} \right)$ t in t $\frac{c_2}{f}$ ttructure with tetrahedral coordinated Cu. ff \overline{f} is in contrast to main group \overline{f} originally high cation-vacancy formation-vacancy formation-vacancy formation-vacancy formation-vacancy formation t $\frac{1}{2}$ for formation energy is the main reason for the main reason energy is the main re

eral tend to be intrinsically finite due to the ease of t tion of cation vacancies as shallow hole producers as shallow hole producers as shallow hole producers and the t \mathbf{f} intrinsic potential potential potential points \mathbf{f}

II. METHODS

 \therefore t for t intrinsic ΔH for various intrinsic various intrinsic various intrinsic various intrinsic various intrinsic various intrinsic various interior interior interior interior interior interior interior interior defects and their ionization energies, as well as defect and carrier concentrations. The formation entitled and *Hf* for *D* tt ft function E_F

$$
\Delta H_{D,} (E_F, \mu) (E_{D,} E_H) + \sum_{\alpha} \alpha (\mu_{\alpha} + \Delta \mu_{\alpha}) + (E_v + \Delta E_F), \qquad (1)
$$

 ttt the state in the state $($ $t \quad f \quad t$ $\mathbf{t} = \mathbf{t}$. Because the Fermi level generally lies in \mathbf{t} to the VBM set $($, the level is not occupied in the level is not occupied in the level is not occupied in the level is t under equilibrium conditions.

V. EQUILIBRIUM CARRIER CONCENTRATION

In order to demonstrate the -type nature, we need to show that hole producers indeed are the domination of the domination of the domination of the domination of th and effective produce holes. Therefore, we evaluate equipment \mathbf{f} lies defect and concentrations that are al[so](#page-3-0) \mathbf{r} tities directly comparable with experiment. Figure shows t the defect concentrations and E_F and E_F and E_F and F_F \mathbf{t} temperature as calculated from the calculated from t simulations. The dominant defect in either t in either t poor growth conditions in the *VCU* hole producer that for the *VCU* hole producer that fo tt 10²⁰ cm − (-)
t t, t _→ tt t t1 (2) ft tttly, is nonstoichiometric, and independent to the *VC*u concentrations are the *VC* contains the copyright observed 1 contains the copyright observed definition 1 between 2×10^{1} and 2×10^{20} cms the f $\left(\begin{array}{cccc} \text{if} & \text{t} & \ldots & \text{t} & \end{array} \right)$ 12 (1) ft et \downarrow than (1) $\begin{array}{cccc} - & (-) & t & \dots & t & t & f t \end{array}$ hole killer $h=10$ ¹ throughout temperature temperat ture range considered. Hence, in all growth conditions, the c dominant defect is the hole producer *d*efect is the hole producer \mathcal{A} for the experimental off-stoichiometry. t room temperature concentrations are determined as t mined by recalculating the $\mathbf{t}=\mathbf{t}=\mathbf{t}=\mathbf{t}$ while maintaining the equilibrium defect concentrations at a given, the temperature temperature. The room temperature t hole concentration for the *V*_Cu contraction of the *V*_C centration, which is the hole concentration at \mathbf{t} the \mathbf{t} th temperature at \mathbf{t} ture \mathbf{I}_g for \mathbf{I}_g the concentration of \mathbf{I}_g concentration at room temperature drops by a few orders of f

magnitude from the carrier concentration at *Tg* because even the *L*_W t

0.2 tt ft ft ⊥_w

= ¹ release the host-derived acceptor level and the host-derived acceptor level acceptor le $\varepsilon(0/-)$ t ft t t t t ϵ . $1\epsilon_0$.

VI. DESIGN RULES FOR *p***-TYPE OXIDE**

The present study demonstrates that -type doping of oxides is the reputation of the reputation between the reputation between \mathbf{r}_i $\mathbf t$ orbitals $\mathbf t$ of $\mathbf t$ is the metal states of $\mathbf t$ of $\mathbf t$ is the metal states of $\mathbf t$ $\begin{array}{cccccccccccccc} t & t & t & & & & & t & t & (2) \\ t & & & -t & & & t & t & & t & ff & t \end{array}$ \mathbf{t} following. \mathbf{f} ensures to the ensuing \mathbf{f} ft the Van State () levels, the cation vacancy creates a delocalized, conductive a delocalized, conductive a delocalized, conductiv \mathbf{t} to the case of \mathbf{t} in the case of \mathbf{t} in the case of \mathbf{t} in the case of \mathbf{t} doping, the high variable is more unlikely that t is that t the intervals installed installed the gap. *Includes* e **b** s **d t b c f 11.1 c f 11.1 c f 11.1 c f 11.1 c f 1**

- *filled* cation shell that lies as high in energy as t -
- $\begin{array}{cccccccccccccccccc} \mathbf{t} & & & & \mathbf{t}\mathbf{f} & & & \mathbf{t} & & \$ $\,$,) tt.

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