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Contribution of electronic entropy to the order-disorder transition of Cu_3Au J. Paras  and A. Allanore *Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA*

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Cu_3Au experiences a phase transition at 662 K from an ordered low-temperature phase to a disordered solid solution. While significant work has been devoted to characterizing the enthalpy of this transition, the apportionment of the entropy has remained out of reach. Current estimates of the vibrational and configurational entropy for the transition are larger than the total entropy of the transition experimentally measured by calorimetry, while calculations of the electronic entropy via *ab initio* methods have remained difficult. This work calculates an electronic entropy difference of -6.29 J/mol K based on a recent formalism that links experimentally measured electronic transport data and equilibrium thermodynamic properties. The application of this formalism brings some estimates of the vibrational and configurational entropy in line with the calorimetrically measured total entropy.

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I. INTRODUCTION

The Cu-Au system exhibits order-disorder transitions that involve the loss of short- and long-range order in low-temperature intermetallic compounds Cu_3Au and CuAu . With increasing temperature, these compounds undergo an order-disorder phase transition, forming a Cu-Au solid solution before melting. An example of a plausible phase diagram for this system is presented in Fig. 1. Although the nature of the phase boundaries remains in dispute, particularly for CuAu_3 , Fig. 1, computed from a database optimized to mimic phase transition boundaries [1], shows the significant off-stoichiometry of the intermetallic compounds and the congruent nature of the order-disorder transition.

The ordered compound Cu_3Au exhibits a first-order phase transition from an L1_2 structure with Cu occupying the face center to a disordered fcc structure at a critical temperature $T_c = 662$ K. The enthalpy of this transition, ΔH^T , was reported by Hultgren to be 4431 J/mol (with mol, in this case, in terms of Cu_3Au formula units), corresponding to a total entropy of transition, ΔS^T , of 6.7 J/mol K [2].

The order-disorder transition in CuAu occurs in two stages. The first transition occurs near 658 K between CuAu(I) and CuAu(II) [3]. CuAu(I) has the L1_0 structure ($P4/mmm$), which forms a superlattice of five repeating unit cells upon transition to CuAu(II) [4,5]. The nature of the $\text{I} \rightarrow \text{II}$ phase transition is disputed and is not depicted in Fig. 1. While a structural view of this transition through transmission electron microscopy (TEM) suggests that this is a second-order

phase transition, calorimetric and electronic transport measurements strongly suggest that the transition is first order [6,7]. Structural disordering of the superlattice CuAu(II) to CuAu(D) occurs at 695 K, where D marks the disordered phase. Careful calorimetric studies propose ΔH^T values and critical temperatures of 651.3 J/mol(CuAu) ($T_c = 670$ K) and 2448 J/mol(CuAu) ($T_c = 695$ K) for the $\text{I} \rightarrow \text{II}$ and $\text{II} \rightarrow \text{D}$ transitions [8]. Estimates of the entropy of the transition vary from 0.84 to 0.97 J/mol(CuAu) K for $\text{I} \rightarrow \text{II}$, and from 3.5 to 5.0 J/mol(CuAu) K for $\text{II} \rightarrow \text{D}$. Use of the word mol here refers to the relevant formula unit of the intermetallic compound, rather than the mol of solution.

There has been some confusion in the literature over the inclusion of changes in the integral thermodynamic properties at the onset of disordering or at the onset of the first-order phase transition. Hultgren notes that Cu_3Au exhibits some form of disordering with an associated change in the heat capacity before exhibiting the identified phase transition [2]. This has contributed to the confusion in the literature over whether the transition is first or second order, or even whether elements of both occur. While some researchers have attempted to quantify a total entropy of disorder by integrating changes in the heat capacity together with the ΔH^T , this approach may obscure the relative significance of the difference in the configurational, vibrational, and electronic degrees of freedom at the phase transition [9]. Additionally, according to the Landau-Lifshitz criterion, a second-order phase transition is forbidden thermodynamically because the star of the wave vectors for the L1_2 ordered phase is the 100 type, and can sum to a $\langle 111 \rangle$ vector, which is a reciprocal lattice vector of the parent fcc phase. This article will therefore focus on quantifying the contribution of the electronic entropy to the measured ΔS^T associated with the first-order transition.

While experimental thermodynamic campaigns have led to improved identification of the CuAu and Cu_3Au phase boundaries and the enthalpic contribution to thermodynamic equilibria, the modeling and partitioning of the entropy have,

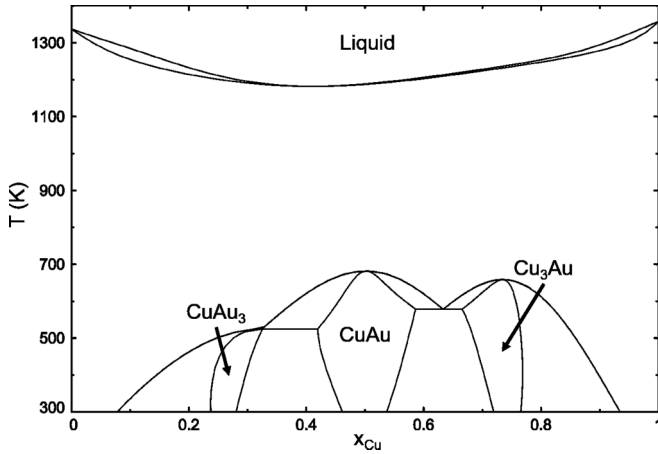


FIG. 1. This phase diagram was computed with the FactSage 7.3 phase diagram module using the SGTE-Bins database [1]. The diagram illustrates the order-disorder transitions of three low-temperature intermetallic compounds to a high-temperature disordered solid solution. Many features of this phase diagram are in dispute, in particular the behavior of CuAu_3 . This diagram is for illustrative purposes only.

so far, remained out of reach [3]. Significant study has been devoted to Cu_3Au in particular, which, therefore, will be the focus of this paper. Limited electronic transport data are available for the CuAu compound, so analysis of this compound is relegated to the Appendix. Due to the dispute over the congruence of its phase transition, CuAu_3 will be excluded from the analysis altogether. The total entropy difference of an order-disorder phase transition is given by the equation

$$\Delta S^T = \Delta S^{\text{vib}} + \Delta S^{\text{config}} + \Delta S^{\text{mag}} + \Delta S^{\text{elec}}, \quad (1)$$

where ΔS^{vib} is the difference in the vibrational entropy upon disordering, ΔS^{config} is the configurational entropy difference, ΔS^{mag} is the magnetic entropy difference, and ΔS^{elec} is the electronic entropy difference. We hypothesize that electronic entropy plays a significant role in the order-disorder transition and that its difference is negative upon transition to the disordered state. The neglect of this has made prior estimates of the vibrational and configurational entropies irreconcilable with the overall entropy reported for the transition.

Resistivity measurements initially made by Bowen in 1954 demonstrated that there was a concomitant change in long-range order and the elastic constants of partially disordered samples of Cu_3Au wire as they were heated and allowed to order [10]. This work suggested that vibrational and configurational entropy were somehow linked and contributed to the thermodynamics of the order-disorder transition in Cu_3Au . Numerous studies have attempted to support this hypothesis through the measurement and calculation of the vibrational entropy difference at the phase transition [11–18]. Estimates of the ΔS^{vib} of Cu_3Au have ranged from 0 to 4.7 J/mol K (or close to zero and slightly negative in the case of Bogdanoff *et al.*), with most being less than 2.7 J/mol K and much closer to zero [13].

The complementary entropy necessary to describe the total phase transition is frequently ascribed to the configurational

entropy increase upon disordering. This assumption may be misleading, as prior estimates of the configurational entropy also exhibit a relatively large range. We will briefly explore this idea.

Assuming that the compound Cu_3Au just below the order-disorder transition temperature is perfectly ordered, its configurational entropy $S_{\text{ordered}}^{\text{config}}$ would be zero. If one assumes that the atomic configurations of the disordered state are themselves completely random, then the difference in configurational entropy associated with the phase transition would be given by the classic expression for the configurational entropy of a fully random solution,

$$\Delta S^{\text{config}} = S_{\text{disordered}}^{\text{config}} = -R(x_{\text{Cu}} \ln x_{\text{Cu}} + x_{\text{Au}} \ln x_{\text{Au}}), \quad (2)$$

where x_{Cu} and x_{Au} are the mole fraction of Cu and Au, respectively. Calculation with Eq. (2) for Cu_3Au yields 18.7 J/mol(Cu_3Au) K [note that the factor of 4 difference from Eq. (2) is to account for the mol of formula unit here]. This is already much larger than the measured transition entropy of Cu_3Au (6.7 J/mol K). There are two possibilities to account for this and satisfy Eq. (1): the electronic and vibrational contributions to the entropy are negative, or the effective difference in configurational entropy is much smaller than the upper-bound estimate provided by Eq. (2).

We can answer the second possibility for the discrepancy in the entropy directly; the assumptions necessary to derive Eq. (2) are known to be untrue near the phase transition in this system. There is some degree of disordering in the low-temperature phase (here, the compound) as it approaches the phase transition, as well as some degree of short-range ordering in the high-temperature phase after the transition. This has been experimentally supported through the measurement of Cowley order parameters, which describe the degree of lattice site randomness in crystalline solids [19–21]. We therefore reconsider Eq. (2) as

$$\Delta S^{\text{config}} = S_{\text{disordered}}^{\text{config}} - S_{\text{ordered}}^{\text{config}}, \quad (3)$$

where $S_{\text{disordered}}^{\text{config}}$ is the configurational entropy of the high-temperature disordered state with some degree of short-range ordering, and $S_{\text{ordered}}^{\text{config}}$ is the entropy of the low-temperature ordered state with some degree of disorder. Whereas Eq. (2) represents the upper-bound estimate of the total difference in configurational entropy for an order-disorder transition, proper evaluation of the terms in Eq. (3) should decrease ΔS^{config} as there is likely considerably greater than zero configurational entropy in ordered Cu_3Au and a degree of order in the solid solution near the phase transition, both of which would lower the calculated configurational entropy of the transition.

Previous work has attempted to address the degree of ordering of each phase through modeling and experimentation [9,15]. These efforts have, so far, proven unable to provide an accurate estimate of the source and apportionment of the entropy at the first-order phase transition of Cu_3Au . Additionally, evaluation of the electronic entropy in [15] uses a formulation of the Sommerfeld model that is only valid at low temperature. It is also not clear whether the use of density functional theory (DFT) to calculate the electronic density of states in a system that exhibits strong interaction among

d -band electrons is even sufficiently accurate to calculate a meaningful electronic entropy, particularly in a system that also exhibits disorder [22]. We therefore propose to study the order-disorder transition of Cu_3Au using a formalism that connects reversible thermodynamics to the measurable transport properties of electrons. We will show that the electronic entropy makes up a significant fraction of the phase transition entropy in Cu_3Au and provides a plausible means to reconcile the computed values for the configurational and vibrational entropy.

II. METHODS

The electronic entropy can be accessed from measurable electronic transport properties. It has been demonstrated that the partial molar entropy of a conduction electron can be related to the Seebeck coefficient from [23,24],

$$\left(\frac{dS}{dn_e}\right)_{T,P,n_j} = -\alpha F, \quad (4)$$

where α is the Seebeck coefficient and F is the Faraday constant.

The integral form of this equation was derived in [25,26] and resulted in the electronic state entropy,

$$S_e = -n_e e \alpha_e, \quad (5)$$

where e is the fundamental charge constant, and n is the number of free charge carriers (here electrons). This is then converted from a volumetric to a molar quantity via the molar volume (V_m),

$$S_e = -V_m n_e e \alpha_e. \quad (6)$$

This formalism has already successfully demonstrated the electronic contribution to the mixing entropy in liquid Te-Tl alloys, as well as the electronic entropy for the metal-insulator transition in VO_2 [26,27]. Hall effect measurements were used in both cases to calculate the conduction charge carrier concentration and will therefore be used in this work. Success in systems that are noncrystalline (liquid Te-Tl) or crystalline with strong electron-electron interaction (VO_2) increase our confidence in the applicability of this formalism to the order-disorder transition in the Cu-Au system.

Hall effect measurements for Cu_3Au were conducted by Elkholy *et al.* as a function of temperature [28]. Their data are reproduced in Fig. 2. The approximate value of the Hall coefficient is $-0.97 \times 10^{-13} \text{ V cm/A Oe}$ just below the phase transition temperature. The Hall coefficient exhibits a discontinuity at the phase transition temperature before assuming a constant value in the disordered state of $-6.75 \times 10^{-13} \text{ V cm/A Oe}$. These characteristic values were chosen because they represent the discontinuity in the extensive properties associated with the first-order phase transition. The sign of both values indicates that at the temperature of the transition, charge transport is electron dominated. This assumption was used to calculate the conduction electron density via the equation

$$n = -\frac{1}{(R_H e)}, \quad (7)$$

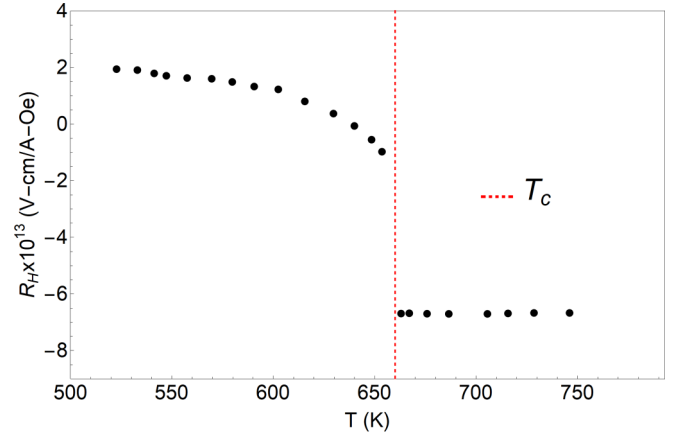


FIG. 2. Variation of the Hall coefficient measurements of Cu_3Au as a function of temperature. A discontinuity is exhibited at the order-disorder transition marked by the dashed line. Reproduced from Ref. [28].

where R_H is the Hall coefficient, e is the fundamental charge, and n is the conduction electron density.

Seebeck coefficient data were also measured as a function of temperature by Airoidi *et al.* for Cu_3Au and exhibited a discontinuity at the phase transition [29]. This data is replotted in Fig. 3. The computed conduction electron densities and electronic entropies, Seebeck coefficient data, and molar volume data are presented in Table I. Reliable molar volume data were unavailable for the disordered state, and so only the molar volume of the ordered state was used to convert between volumetric and molar quantities. Because the lattice constant of quenched, disordered samples of Cu_3Au is within 1% of the ordered value, we believe this assumption will not affect the conclusions drawn in this paper [11].

The values of the Seebeck coefficient from Airoidi *et al.* [29] were taken at the discontinuity in the measurement that occurred at the transition temperature, again because this represents the discontinuity in extensive quantities associated with the first-order phase transition.

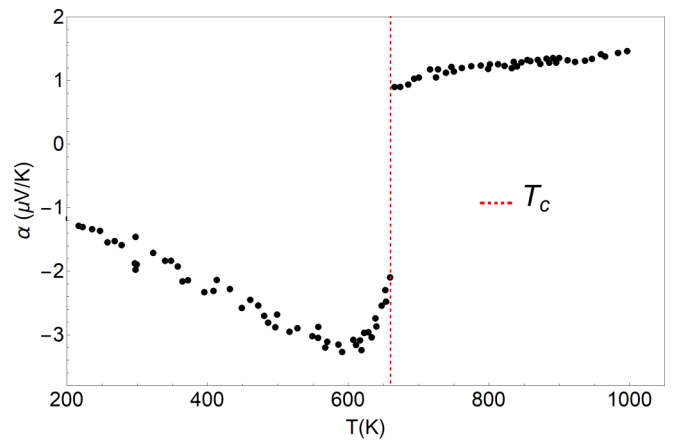


FIG. 3. Variation of the Seebeck coefficient as a function of temperature for the Cu_3Au compound. The discontinuity occurs at the order-disorder transition temperature. Reproduced from Ref. [29].

TABLE I. Electronic properties of the Cu₃Au intermetallic compound in the ordered and disordered states.

T_c (K)	α^{dis} ($\mu\text{V/K}$)	α^{ord} ($\mu\text{V/K}$)	V_m ($\frac{\text{cm}^3}{\text{mol}}$)	n_e^{dis} (m^{-3})	n_e^{ord} (m^{-3})	S_e^{dis} (J/mol K)	S_e^{ord} (J/mol K)
662 [3]	1.4 ^a [29]	-1.7 [29]	32 [31,32]	9.25×10^{28} [28]	6.46×10^{29} [28]	-0.68 This work	5.6 This work

^aThe absolute value of thermoelectric coefficients before 1977 was found to be in error by about $0.3 \mu\text{V/K}$. These values have been corrected using a new absolute Seebeck coefficient scale [30]. This has little effect on the conclusions drawn in this paper.

III. RESULTS

The results for the calculated electronic entropy of the order-disorder transition in Cu₃Au are presented in Table II and compared to prior calculations of the vibrational and configurational entropy.

It is found that the electronic entropy in Cu₃Au could bring prior estimates of the vibrational and configurational entropies into reasonable agreement with the calorimetrically determined transition entropy. The total entropy of the transition is 6.7 J/mol K. The range of values for $\Delta S^{\text{vib}} + \Delta S^{\text{config}}$ is 9.9–14.6 J/mol K. Including the electronic entropy, this range adjusts to 3.61–8.11 J/mol K, with the uncertainty coming from different prior estimates of the vibrational entropy difference.

If the electronic and configurational entropies cited are taken to be correct, a value of ~ 3.1 J/mol K for the vibrational entropy would render the total entropy consistent with the calorimetrically measured value. This estimate of the vibrational entropy falls within the bounds proposed in the literature. Because the electronic entropy does not presently account for the total transition entropy alone, discussion of its relation to other components of the entropy is warranted.

IV. DISCUSSION

The configurational entropy was calculated via measured long-range and short-range order parameters using formalisms developed by Fowler and Guggenheim, Crowley, and Takagi [20,21,33]. While various degrees of order across the phase transition decrease the configurational entropy of the transition from the upper-bound estimate in Eq. (1), the configurational entropy value cited in Table II is still significantly larger than the total phase transition entropy without considering the addition of any vibrational entropy differences.

Crombie *et al.* highlights that the nonconfigurational entropy must be negative to remain self-consistent with calorimetric measurements [19]. While there has been disagreement over the relative importance of the vibrational entropy, estimates have remained largely positive. Heuristically, this strongly suggests that the electronic entropy of the transition

must be negative. Evaluation of the presented formalism for the transport electronic entropy, when considered in conjunction with the range of configurational and vibrational entropy terms, brings the total transition entropy in line with the calorimetric value.

While this broad agreement is reassuring, we recognize that there has been some dispute over the possibility that the electronic entropy formalism in Eq. (5) can (and, in this case, does) produce a negative state electronic entropy. This is a problem in metals that exhibit negative Hall coefficients (which indicates electron transport) with positive Seebeck coefficients, which typically would indicate hole conduction.

We have identified two possibilities to explain this apparent discrepancy: the state electronic entropy in disordered Cu₃Au is indeed negative or the observed Hall effect and Seebeck coefficient are not indicative of the electron (and hole) concentrations and resulting entropies. While both remain a possibility, we shall demonstrate that the first scenario is still consistent with band theory and will examine the implications of the second scenario.

Here, a negative electronic entropy in the disordered state was found by assuming that the disordered alloy exhibited electron dominated transport. We shall present an argument found in work by Rockwood that demonstrates that the partial molar entropy of an electron may indeed be negative and can be self-consistent with band theory [34]. After Eq. (4) was initially defined, the state electronic entropy was calculated from the partial molar electronic entropy \bar{S}_e , given in Eq. (5) from work by Rinzler and Allanore [25,26]. Whereas solution theory is often applied to systems with changing composition, the formalism in this paper assumes that one can describe a phase as itself a solution of atoms and electrons. Naturally, there should be a counterpart to \bar{S}_e associated with the atoms which would include the core electrons and the atomic nuclei. This term would include vibrational and configurational components of the entropy as well as any other degrees of freedom associated with the core electrons. We will call it \bar{S}_{atom} .

The equation for the total entropy of the phase would then be given by

$$S^{\text{Total}} = n_e \bar{S}_e + n_{\text{atom}} \bar{S}_{\text{atom}}. \quad (8)$$

TABLE II. Electronic entropies of the transition for Cu₃Au. Here, mol is in terms of the mol of compound Cu₃Au.

T_c (K)	ΔS^{T} (J/mol K)	ΔS^{elec} (J/mol K)	ΔS^{vib} (J/mol K)	ΔS^{config} (J/mol K)
662 [3]	6.7 [2]	-6.29 This work	null-4.7 [11–18]	9.9 [19]

We do not suggest that the total entropy of a phase given by Eq. (8) may be negative, but assert that the partial molar entropy of metallic phases may. And, indeed, there are examples of negative partial molar properties for metallic systems [35].

We turn our attention towards band theory. The Sommerfeld model offers a useful point of comparison between the presented thermodynamic formalism of the electronic entropy and band theory. Consider the electronic heat capacity in the Sommerfeld model for a metal as [36]

$$C_{v,\text{electronic}} = \frac{\pi^2}{3} k_b^2 T g(\varepsilon) = K_1 T g(\varepsilon), \quad (9)$$

where K_1 is just a constant. Integration of this equation from zero Kelvin by temperature to get the total electronic entropy gives

$$S_{\text{electronic}} = K_1 T g(\varepsilon). \quad (10)$$

Here it is assumed that the temperature range is such that $C_v \sim C_p$ (where C_p is the constant pressure heat capacity) and that the electron density of states does not change significantly with temperature itself.¹ The partial molar entropy of an electron would thus be the partial derivative of the integral property [as in Eq. (10)] and this should then be equal to Eq. (4) via

$$\bar{S}_{\text{electronic}} = -\alpha F = \left(\frac{\partial S}{\partial n_e} \right)_{T,P,n_j} = \left[\frac{\partial K_1 T g(\varepsilon)}{\partial n_e} \right]. \quad (11)$$

Applying the chain rule to the right-hand side of Eq. (11), we have

$$\bar{S}_{\text{electronic}} = -K_1 T \left[\frac{\partial g(\varepsilon)}{\partial \varepsilon} \right] \left(\frac{\partial \varepsilon}{\partial n_e} \right), \quad (12)$$

where we take the definition of the electronic density of states to be

$$g(\varepsilon) := \frac{\partial n_e}{\partial \varepsilon}. \quad (13)$$

Therefore,

$$\bar{S}_{\text{electronic}} = \frac{K_1 T}{g(\varepsilon)} \left[\frac{\partial g(\varepsilon)}{\partial \varepsilon} \right]. \quad (14)$$

Equation (14) suggests that the density of states of disordered Cu₃Au at the transition temperature would have a negative slope with energy. We want to be clear, however, that consistency with band theory may neither be necessary nor desirable. The conversion of density functional theory (DFT) calculated band structures from a k -point grid to a density of states requires an energy broadening scheme to interpolate between the different k points. These schemes are often chosen

qualitatively to avoid smearing out important features of the band structure while also avoiding the introduction of spurious noise into $g(\varepsilon)$.

There are several other concerns that we have when using $g(\varepsilon)$ as a thermodynamic descriptor. Most calculations do not modulate the density of states as a function of temperature, but rather leave that to the Fermi-Dirac distribution. Computing the electronic entropy from $g(\varepsilon)$ in this manner would only meaningfully include the configurational entropy of electronic ground states. There is evidence in the literature that this is not true [37].

Because the Kohn-Sham states themselves are not the strict electronic states of the system and DFT has great difficulty with correctly calculating excited states, let alone for disordered systems, one can readily see how these types of calculations may fall short of the necessary precision to demonstrate the importance of the electronic entropy as a function of temperature. Therefore, we posit that the incomplete description of electron thermodynamics provided by $g(\varepsilon)$ may explain the consistent underestimation of the contribution of the electronic entropy in real materials vis-à-vis the transport property method implemented in this paper. Whereas we believe our method quantitatively captures all the possible excited states not captured by the density of states (DOS) produced via energy minimization techniques, particularly at finite temperature [25,27].

We acknowledge that there is still the possibility that the Hall effect and Seebeck measurements in the disordered state may obscure some of the electronic entropy. A positive Seebeck coefficient is indicative of hole conduction and is self-consistent with a commensurate reduction in the Hall coefficient. In a simple two-band model wherein one of those bands is hole dominated, the overall Seebeck coefficient is weighted by the conductivity of their respective bands and is given by the equation

$$\alpha = \frac{\sigma_n \alpha_n + \sigma_p \alpha_p}{\sigma_n + \sigma_p}. \quad (15)$$

Equation (15) would imply that in such a model, the effective hole conduction would be greater than the electron contribution to the conductivity. If, in the typical case, the sign of the Seebeck coefficients differs between the two bands, Eq. (5) would require revision as

$$S_e = -n_n e \alpha_n + n_p e \alpha_p. \quad (16)$$

This may result in an increase in the electronic entropy estimate for the disordered state. However, we believe it is still unlikely that it changes the conclusions of this paper. First, we expect a breakdown in Bloch's theorem in the disordered state, and a decrease in the effective free carrier concentration, which is what is experimentally observed by an increase in the magnitude of the Hall coefficient upon disordering (Fig. 2).

¹ A bold and often incorrect assumption.

TABLE III. Electronic entropies of the transition for CuAu. Here, mol is in terms of the mol of the compound CuAu.

Transition	T_c (K)	ΔS^T (J/mol K)	ΔS^{elec} (J/mol K)	ΔS^{vib} (J/mol K)	ΔS^{config} (J/mol K)
CuAu(I) → CuAu(II)	658	0.84–0.97 [2,8]	–1.13		
CuAu(II) → CuAu(D)	683	3.5–5.0 [2,8]	0.96	3.0 [17]	9.9 [19]

TABLE IV. Material transport property dated used for the calculation of the electronic entropy in CuAu.

Phase	α ($\mu\text{V/K}$)	V_m (cm^3/mol)	n_e (m^{-3})	S_e (J/mol K)
CuAu(I)	0.56 [40]	17.355 [4]	1.82×10^{29}	-0.28
CuAu(II)	4.37		1.2×10^{29}	-1.42
CuAu(D)	1.94		8.49×10^{28}	-0.45

There is also evidence to suggest that such sign discrepancies between the Hall effect and Seebeck coefficient in metals could be due to a nonconstant electron relaxation time, which can lead to positive Seebeck coefficients in materials that are dominated by electron conduction [38]. In which case, our assumption surrounding conduction dominated by electrons is correct.

Whereas in Cu_3Au , the apparent impact of such a Seebeck-Hall effect sign discrepancy on the magnitude of the electronic entropy difference is likely small, in CuAu, the magnitude of the computed electronic entropies is of a similar magnitude. This would prove problematic for the computation of the electronic entropy in CuAu if our assumptions of carrier dominance were to be incorrect. CuAu therefore represents an ideal test case for future research to explore what, if any, impact the Seebeck-Hall effect sign discrepancy has on the entropy of metals and alloys. The definitive experiment would involve measuring the α_n and α_p of CuAu, as well as the electron and hole occupancy of the bands from which these partial Seebeck coefficients arise. Comparison of the resulting calculations for the electronic entropy with what has been calorimetrically determined for the total phase transition could determine whether such extensive characterization is necessary to compute compound and solution thermodynamic properties.

Ultimately, we are reassured that in ordered Cu_3Au , the Hall and Seebeck measurements both indicate electron transport and that the electronic entropy is significantly larger than in the disordered state. This increases the likelihood that the electronic entropy of the transition is still negative even if the assumptions surrounding the complexity of electronic transport in the disordered state are incorrect.

V. CONCLUSION

The electronic state contribution to the order-disorder transition entropy in Cu_3Au was evaluated and found to be -6.29 J/mol K. The electronic entropy contributed significantly to the phase transition total and provides a plausible

account for the total measured entropy of the transition in conjunction with the vibrational and configurational entropy differences. We propose a value of 3.1 J/mol K for the vibrational entropy of the transition that would be self-consistent with our calculations.

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APPENDIX

CuAu exhibits a sign discrepancy between its Hall effect measurements and the Seebeck coefficient throughout the temperature range of interest. Therefore, there is a stronger possibility that the source of this discrepancy may manifest in an electronic entropy equation akin to Eq. (16) and that assumptions over single carrier dominance may result in erroneous estimates of the electronic entropy. Additionally, the estimates of the vibrational entropy difference between the ordered and disordered phases in CuAu are incomplete as there is more than one phase transition before full disordering. We therefore decline to draw stronger conclusions about this material and instead include calculations of the electronic entropy of CuAu based on the available literature data for completeness. Hall effect data were used to calculate the conduction electron density via Eq. (6) from data taken from Sidorov [39].

The as-calculated electronic entropy represents a significant fraction of the total phase transition entropy reported for the two phase transitions of CuAu. The relevant values are provided in Table III.

The data necessary to make these calculations are provided in Table IV. We find that in all states, the electronic entropy is negative. If the assumptions surrounding this electronic entropy calculation in CuAu are correct, this suggests a negative sloping electronic density of states with increasing energy in all phases of CuAu.

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