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Letter

Intercalate Superconductivity and van der Waals Equation

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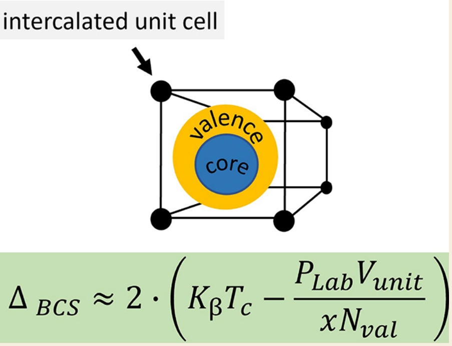
ABSTRACT: Superconductivity in two single-element intercalated compounds has been investigated with the van der Waals equation. For Cu_xTiSe_2 and $YBa_2Cu_3O_{6+x}$, the van der Waals term characterizing the attractive energy per particle (i.e., electrons), aN/V, is calculated from concentration-dependent transition temperature plots derived from experiment. It is shown that two times the attractive energy per intercalant valence electron ($2aN_{\text{val}}/V_{\text{unit}}$) is equal to the energy gap predicted by BCS theory (Δ) for these superconductors. This realization allows another way to estimate the energy gap of superconducting intercalated insulators and semiconductors, this time, directly from physical real-space properties of the superconductor and the applied external pressure. The physical properties of importance are shown to be the intercalant concentration, transition temperature, and the number of intercalant valence electrons per unit cell volume.



KEYWORDS: *superconductivity, intercalation, ideal gas law, van der Waals equation, insulator, semiconductor, BCS theory*

■ INTRODUCTION

BCS theory[1] developed by Bardeen, Schrieffer, and Cooper, revealed paired electrons responsible for superconductivity. The pairing was shown to arise from a nonzero attractive potential, regardless of the attractive potential's mechanism of emergence. In turn, the famous result for the energy gap in the weak coupling limit for electron−lattice interactions was predicted to be $\Delta = 1.764K_{\beta}T_c$. Much research has verified the existence of the BCS gap measured by various experimental techniques such as specific heat capacity (SHC),[2−4] angle-resolved photoemission spectroscopy,[5,6] and Raman scattering.[7−9] For intercalated insulators and semiconductors, estimated gaps from experiment and BCS theory generally agree especially at "optimum" doping, which is usually associated with the highest concentration-dependent transition temperature. For Cu_xTiSe_2 and $YBa_2Cu_3O_{6+x}$, optimal concentrations are $x \approx 0.08$ ($T_c \approx 3.8$ K) and $x \approx 0.98$ ($T_c \approx 90$ K), respectively.

A more recent study on the emergence of superconductivity from intercalated compounds, specifically at the insulator−superconductor boundary of those intercalated by a single element, revealed the boundary closely follows the ideal gas law relation, as shown in eq 1.[10] Where P and V_{unit} are the pressure (1 atm) and unit cell volume, respectively. The variables x_{onset}, N_{val}, K_{β}, and $T_{\text{c-onset}}$ are the minimum intercalant concentration required for superconductivity to emerge such that $T_c \neq 0$ at constant pressure, the number of valence electrons of the intercalant (including s and d electrons for transition metals), Boltzmann constant, and the experimentally measured transition temperature at x_{onset}, respectively. This is essentially the classical ideal gas law equation in terms of T_c and real-space physical properties. Keep in mind that directly using the ideal gas equation to empirically represent an electron's behavior is quite unconventional; additionally, it is not traditionally used to describe phase transitions. On the contrary, the ideal gas law is typically applied to classical objects with physical volume, such as atoms and molecules, within specific ranges of temperatures, pressures, and densities.[11] Now it is shown to empirically embody the behavior of intercalant valence electrons at the insulator−superconductor boundary, while aiding in the prediction of the onset of superconductivity, as well.[10]

$$PV_{\text{unit}} \approx x_{\text{onset}} N_{\text{val}} K_{\beta} T_{\text{c-onset}} \tag{1}$$

Although the ideal gas law relation is a close approximation for onset conditions, it is not exact.[10] Therefore, the aim of this report is to apply the extended ideal gas law equation (van der Waals equation) to superconducting intercalated compounds to gain insight on the reason for the apparent deviation from eq 1. Special attention is placed on the pressure parameter "P" to reveal the attractive interactions among superconducting intercalant valence electrons. It will be shown that the estimated van der Waals attractive energy of two intercalant valence electrons in the superconducting state is equal to the calculated and measured BCS gap for $x \geq x_{\text{onset}}$.

Intercalated compounds Cu_xTiSe_2 and $YBa_2Cu_3O_{6+x}$ will be used to accomplish the above tasks. These were chosen as representatives from the list of 40 intercalated compounds

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whose onset conditions were previously shown to be easily modeled by the ideal gas law equation.[10] Although the proposed argument in upcoming sections holds for all 40 compounds, only Cu_xTiSe_2 and $YBa_2Cu_3O_{6+x}$ will be discussed in this article. This is because they appear quite different from each other at first glance. Cu_xTiSe_2 adopts a trigonal structure and is an electron-doped system with BCS-type low-temperature transitions (T_c < 4 K) to superconductivity, whereas $YBa_2Cu_3O_{6+x}$ is a defect perovskite, hole-doped system with non-BCS high-temperature transitions (T_c < 90 K) to superconductivity.[12,13] Though different, they are similar (and comparable to the other earlier reported 38 intercalated compounds) because superconductivity emerges after the single-element intercalation of parent compounds (e.g., $TiSe_2$ and $YBa_2Cu_3O_6$) which have no or low density of states at the Fermi level (e.g., insulator, semiconductor, and low density semimetals). Therefore, the goal is to show that, although they are drastically different from each other, attractive interactions in their superconducting states can still be understood with the same phenomenological model (van der Waals relation), thereby extending the prior utilized model of the ideal gas equation.

VAN DER WAAL'S ATTRACTION AND DISCUSSION

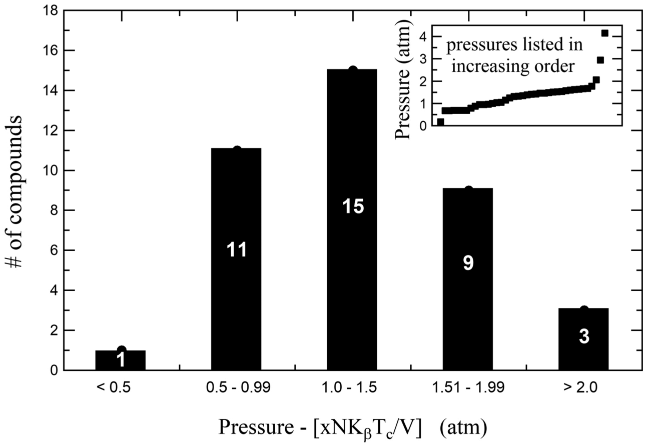

Figure 1. Number of intercalated compounds vs calculated pressure P. Calculated P for 39 previously reported superconducting intercalated compounds,[10] centered around 1.33 atm and grouped in ∼0.5 atm intervals. Refer to Tables 1 and 2 of the Supporting Information for the list of compounds and the variables used to calculate P.

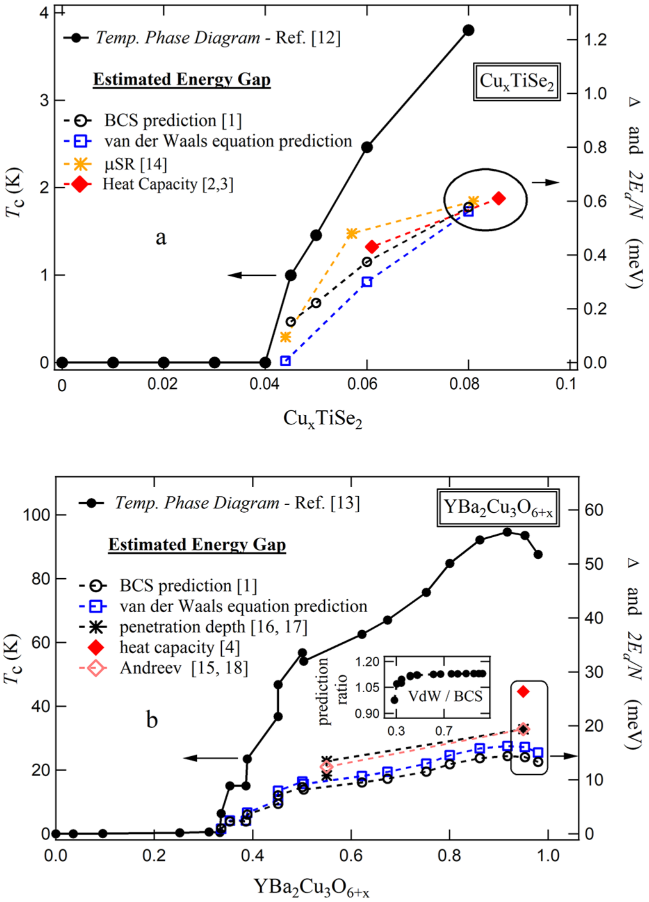

Figure 2. Concentration dependence of transition temperature, BCS gap, and van der Waals prediction. Data for Cu_xTiSe_2 are shown in plot (a). Left axis represents transition temperature T_c, and right axis represents BCS gap (Δ from theory, μSR, and specific heat capacity) and two times the van der Waals energy ($2E_a/N$). Both axes are concentration-dependent. Circle near $x = 0.08$ indicates convergence of data between theory and experiment at optimal doping. Data for $YBa_2Cu_3O_{6+x}$ are shown in plot (b). Left axis represents transition temperature T_c, and right axis represents BCS gap (Δ from theory, Andreev reflection, penetration depth, and specific heat capacity) and two times the van der Waals energy ($2E_a/N$). Both axes are concentration-dependent. Inset depicts the ratio between van der Waals prediction and BCS theory.

Table 1. Cu_xTiSe_2 Doping and BCS Gap

Cu_xTiSe_2	BCS gap = Δ (meV)[a]	
T_c (i.e., doping)	SHC	μSR
≈1 K (x = 0.045)		0.095[15]
2.8 K (0.057 ≤ x ≤ 0.061)	0.43[2]	0.48[15]
3.8 K (optimal)	0.61[3]	0.6[15]

[a] BCS gap (Δ) values shown were obtained using specific heat capacity (SHC) and muon spin resonance (μSR) measurements.

As an example use of the ideal gas law equation, the parameters to estimate the onset transition temperature for $TiSe_2$ intercalated with copper (Cu_xTiSe_2[12]) are P = 1 atm, V_{unit} = 65 Å^3, x_{onset} = 0.045, and N_{val} = 11. This yields from eq 1 an onset transition temperature of 0.96 K, which is close to the measured value $T_{c\text{-onset}}$ = 1 K. Similarly, most transition temperatures calculated from the ideal gas law equation were lower than those from experimentally measured $T_{c\text{-onset}}$.[10] This was perhaps due to a misunderstanding of the pressure variable P which was fixed to 1 atm (i.e., the lab pressure during experiment). If pressure is not held constant, but instead calculated, an interesting feature emerges from the data. Assuming experimentally observed variables V_{unit}, x_{onset}, N_{val}, and the resultant $T_{c\text{-onset}}$ are accurate and necessary to explain the previously reported empirical finding, most calculated pressures ($xN_{val}K_BT_{c\text{-onset}}/V_{unit}$) are greater 1 atm, as shown in Figure 1. The average calculated pressure is 1.33 atm. This suggests the pressure "felt" by intercalant valence electrons at the onset of superconductivity is higher than the background pressure applied by the lab itself (1 atm) during measurement.

By extending the ideal gas law to the van der Waals equation shown in eq 2, the extra pressure above P = 1 atm that intercalant valence electrons experience can be seen as a result of attractive interactions among themselves. To see this, first "$x_{onset}N_{val}$" is rewritten as "N", and for clarity, long subscripts are removed from variables for the remainder of the report but are

Table 2. YBCO Doping and Coupling Ratio

YBCO	coupling ratio = $2\Delta/K_\beta T_c$[a]		
T_c (i.e., doping)	Andreev reflection	λ	SHC
62.5 K ($x \approx 0.55$)	4.6[16]	5[17] and 4[18]	
90 K (optimal)	5[19]	5[18]	6[4]

[a] Strong coupling ratio ($2\Delta/K_BT_c$) values shown were obtained from reflection, penetration depth, and specific heat capacity measurements.

reintroduced toward the end. As a result, aN^2/V^2 (eq 2 rewritten as eq 3) represents the additional pressure (P_a) due to attractive interactions, while repulsive interactions are accounted for by bN. This is the standard van der Waals representation of attractive and repulsive forces.[14] For electrons, $b = 0$ as they are without volume as point particles. The variable P_L represents the pressure on intercalant valence electrons caused by the lab.

$$\left(P_L + \frac{aN^2}{V^2}\right)(V - bN) = NK_\beta T_c \tag{2}$$

$$\frac{aN^2}{V^2} = \frac{NK_\beta T_c}{V} - P_L \coloneqq \boldsymbol{P_a} \tag{3}$$

To see how the attractive interaction relates to BCS theory, one must first multiply eq 3 by V to yield the overall attractive energy (aN^2/V defined as E_a) contained within a unit cell shown in eq 4.

$$\frac{aN^2}{V} = NK_\beta T_c - P_LV \coloneqq \boldsymbol{E_a} \tag{4}$$

Subsequently, dividing eq 4 by N yields the attractive energy per electron (aN/V defined as E_a/N) shown in eq 5.

$$\frac{aN}{V} = K_\beta T_c - \frac{P_LV}{N} \coloneqq \frac{\boldsymbol{E_a}}{\boldsymbol{N}} \tag{5}$$

The result of two times eq 5, the attractive energy between two intercalant valence electrons, is summarized in Figure 2 for compounds Cu_xTiSe_2 and $YBa_2Cu_3O_{6+x}$. Data needed for eq 5 can be found in Supporting Information. The left axes in Figure 2 depict previously reported transition temperatures.[12,13] The right axes represent two times eq 5 calculated for various concentrations (x) at associated transition temperatures (T_c) and the binding energy of two electrons predicted by BCS theory ($\Delta = 1.764K_\beta T_c$). These are compared to energy gaps estimated from various experimental techniques summarized in Tables 1 and 2. Remarkably, estimates from BCS theory and the van der Waals equation generally agree and converge to measured values at optimal doping, as indicated in Figure 2a,b. The inset of Figure 2b depicts the ratio of about 1.1 between the van der Waals prediction and BCS theory for $YBa_2Cu_3O_{6+x}$.

To this end, the van der Waals equation appears to encapsulate a key insight of BCS theory involving the binding energy of pairwise electrons, manifesting itself around the onset of superconductivity as the ideal gas law,[10] where attractive interactions are minimal yet present. These results imply all valence electrons of the intercalant should be considered when discussing intercalate superconductivity. Usually this is not the case. For example, for copper and oxygen, the former is often treated as either a divalent or monovalent element,[20,21] and the latter is typically framed as a "hole dopant".[13] Neither of these scenarios were considered when employing the ideal gas law[10] at the onset or when using the van der Waals equation to estimate the gap (summarized in Figure 3). In both cases, $N_{val} = 11$ was used for copper and $N_{val} = 6$ for oxygen.

It should be noted that the idea of a mechanism giving rise to the apparent attraction among intercalant electrons is not addressed in this report. Yet and still, the van der Waals relation seemingly connects the earlier reported ideal gas model[10] for intercalated compounds to their energy gaps predicted by BCS theory. Though suggestive, one should not simply assume a van der Waals-type interaction (i.e., dispersion-like force) among intercalant electrons as there is no basis for such interpretation from literature or in this report. Thus, the van der Waals equation in relation to superconducting intercalated compounds should only be viewed as a phenomenological model unless proven otherwise.

To further evaluate the new gap equation shown in Figure 3, concentration-dependent gap measurements at constant pressures away from 1 atm are required. As it stands, the new gap equation reproduces expected results specifically at 1 atm for intercalated compounds whose onset conditions follow the ideal gas equation. In the meantime, applying other corrections to the ideal gas law other than the van der Waals equation might afford even more fruitful insights on the superconductivity of intercalated compounds. These corrections may also help predict phase diagrams more accurately than what was shown when the ideal gas law was employed.[10] For example, the virial expansion of the ideal gas law which considers corrections in terms of density (N/V) could potentially be useful in this regard.

CONCLUSION

The van der Waals equation seems to be a good classical model for describing superconducting intercalated compounds. This work fortifies the idea that attractive interactions among electrons are responsible for superconductivity. Consequently, BCS theory's energy gap shows glimpses and hints at the importance of the ideal gas law equation at low doping (i.e., onset conditions). Ultimately, this report coupled with another[10] suggests intercalate superconductivity depends on the intercalant's total valence number, e.g., $N_{val} = 11$ for copper.

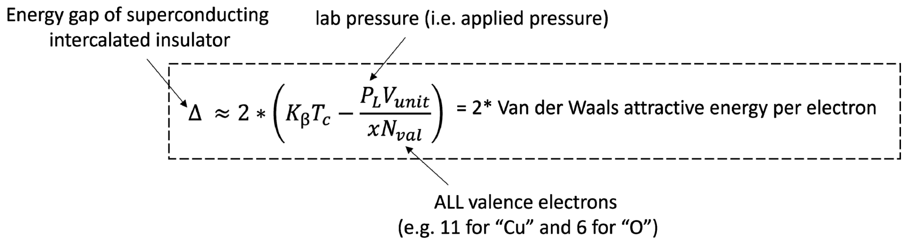

Figure 3. Image depicts the relationship between BCS gap and van der Waals attractive energy per electron for superconducting intercalated compounds. Variable x is the input, T_c is the output, and the constants are P_L, V_{unit}, and K_B.

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ASSOCIATED CONTENT

Supporting Information

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Data used for eq 5 and Figure 1 (PDF)

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Notes

The author declares no competing financial interest.

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