Interacting Electrons in Two-Dimensional Electride Ca$_2$N

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ABSTRACT: We investigated the role of correlation effects in the formation of the spectral and magnetic properties of two-dimensional electride Ca$_2$N. Using the combination of Density Functional Theory with Dynamical Mean-Field Theory (DFT+DMFT), we found that Coulomb interactions between the electrons of the electride states cause a strong renormalization and shift of the energy bands near the Fermi level. Besides, the electronic correlations lead to a competition between the Stoner-type ferromagnetic instability and the antiferromagnetic interactions of the localized moments. The observed patterns should be inherent to other isostructural electrides.

INTRODUCTION

The term “electrides” coined by James Dye represents a rather broad class of materials that have electrons confined in the interstices of the crystal structure. The topology and dimensions of these cavities determine primarily the properties of anionic electrons, including the mobility and degree of localization, especially if the energy bands of these excess electrons cross the Fermi level. These electrons can participate in complex interactions with each other and with cations. As a result, electrides exhibit diverse properties, providing a rich field for experiments and a challenge for theoretical research. A high density of anionic electrons and low binding energy make such materials very promising for a variety of practical applications, particularly as efficient electron emitters and high-performance catalysts.

When a new class of low-dimensional electronic systems with a layered structure was discovered, the first among them, dicalcium nitride, immediately attracted the attention of researchers. Recently, the existence of several two-dimensional electrides isostructural to Ca$_2$N has been confirmed, including Sr$_2$N, Ba$_2$N, Sc$_2$C, Cd$_2$C, Tb$_2$C, Dy$_2$C, Ho$_2$C, and Y$_2$C. Dicalcium nitride is a two-dimensional electride (Q2DE) with the chemical formula [(Ca$_2$N)$^+$] with its space group. The band structure calculations for this system show that a single band with a width of 2.5 eV which crosses the Fermi level $E_F$ consists mainly of nonatomic electronic states (collective oscillations of the density of the free electron gas), revealed using the first-principles time-dependent density functional theory calculations, is striking contrast with what could be expected for a homogeneous electron gas. The temperature dependence of the resistivity of Ca$_2$N is quadratic, which indicates the presence of Coulomb interactions between the electrons responsible for the transport properties. The measurements of the anisotropic magnetoresistance make it possible to argue that the electron—electron interaction in Ca$_2$N is stronger than in metallic Ca because the electrons do not propagate over the entire crystal but are localized in a much tighter space. The experimental data demonstrate a large enhancement of the effective electron mass, 1.9–2.5$m_e$, in Ca$_2$N. The band structure calculations for this system show that a single band with a width of 2.5 eV which crosses the Fermi level $E_F$ consists mainly of nonatomic electronic states centered between the [Ca$_2$N]$^+$ layers with small contributions from the atomic orbitals of Ca and N. This indicates that the electrical conductivity of Ca$_2$N is due to the electrons enclosed in the space between the layers. The experimental work has shown that the results of DFT calculations do not correctly describe the positions of the energy bands that do not coincide well with the angle-resolved photoemission spectroscopy.
(ARPES) results. Thus, the available data indicate that Ca$_2$N can behave as a strongly correlated material and it is important to understand how the Coulomb correlations affect the physical properties of Ca$_2$N, as well as other isostructural electrides. Unfortunately, there is no direct experimental evidence of the presence of magnetic moments in Ca$_2$N. Since correlations are expected on electrode states which are localized between atomic layers, and their wave functions are a combination (superposition) of atomic ones, the magnetic properties and behavior of electrons should be different from what we expect for well-localized d- or f-electrons. In its turn, it makes it difficult to apply standard experimental methods to estimate the magnitude of local magnetic moments.

In the present paper we evaluate the strength of the Coulomb interactions of anionic electrons and investigate the influence of correlation effects on the spectral and magnetic properties of the two-dimensional electrode Ca$_2$N.

**METHODS**

In the present study we used the combination of DFT and DMFT methods which provides the most unambiguous way to investigate the electronic structure. The DFT calculations were carried out with VASP and Quantum ESPRESSO packages, using the PBE exchange-correlation functional. The results of the latter were used to construct the Hamiltonian in the Wannier function (WF) basis using the Wannier90 package for extraction the noninteracting GGA Hamiltonian $H_{\text{GGA}}$, in the real space and transformation to the reciprocal space. The VASP package was used for the estimation of the Coulomb $U$ parameter using a localized basis of atomic orbitals by the linear response approach. Coulomb correlations were taken into account for the constructed Hamiltonian within the DFT+DMFT approach.

This method allows taking into account many-body effects such as Coulomb correlations within the dynamical mean-field theory (DMFT). On the first step an effective Hamiltonian $H_{\text{DFT}}$ was constructed on the basis of the Wannier functions using realistic noninteracting band structure $\varepsilon(k)$ obtained within the DFT for the compound under consideration. Finally, full many-body Hamiltonian which is solved within the DFT+DMFT approach:

$$\hat{H} = \hat{H}_{\text{DFT}} - \hat{H}_{\text{DC}} + \frac{1}{2} \sum_{i,m,\sigma} U_{i,m,\sigma}^\dagger \hat{n}_{i,m,\sigma} \hat{n}_{i,m,\sigma}$$

(1)

Here $U_{i,m,\sigma}$ is the Coulomb interaction matrix and $\hat{n}_{i,m,\sigma}$ is the occupation number operator for the correlated electrode electrons with orbital and spin indices $i,m,\sigma$ at the $i$th site. The elements of $U_{i,m,\sigma}$ matrix were parameterized by the on-site Hubbard parameter $U$ and Hund’s intra-atomic exchange $J_H$ according to the procedure described in ref 35. Since the electrode state is nondegenerate and has only two spin–orbitals $J_H$ was set to 0 eV in the present calculations for the sake of simplicity.

The DFT+DMFT calculations were performed for the inverse temperature values $\beta$ from 2 to 90 eV$^{-1}$, where $\beta = 1/k_BT$, $k_B$ is the Boltzmann constant, and $T$ is the absolute temperature. We used the simplified fully localized limit form for double-counting correction: $H_{\text{DC}} = \hat{U}(N - 1/2)\hat{I}$ in a self-consistent DMFT loop, where $N$ is the total self-consistent number of electrons on the electrode state obtained within the DFT+DMFT, $\hat{U}$ is the average Coulomb parameter for the electrode shell, and $\hat{I}$ is the identity operator. The continuous-time quantum Monte Carlo hybridization expansion solver from the AMULET package was applied to solve the effective DMFT quantum impurity problem. The analytical continuation of the self-energy dependence on the real frequencies was obtained by using the Padé approximation method.

**RESULTS AND DISCUSSION**

To describe the electronic states localized between the atomic layers, we used the maximally localized Wannier functions (MLWFs). Four MLWFs were constructed within the energy window spanned by one energy band crossing the Fermi level and three lower-energy bands (Figure 1a). The first obtained MLWF is centered in the crystal void at position (0.5, 0.5, 0.5), has the symmetry of an s-orbital (Figure 1b), and represents the electrode state. The Ca and N atoms are shown in red/purple and orange, respectively.

![Figure 1](https://doi.org/10.1021/acs.jpcc.1c04485)

Figure 1. (a) Band structure of Ca$_2$N (black lines). The contribution to the Bloch states by the maximally localized Wannier function with s-symmetry centered on the electrode layers is shown in yellow. High-symmetry points in the Brillouin zone correspond to the rhombohedral unit cell. (b) Spatial distribution of the MLWF describing the electrode state. The Ca and N atoms are shown in red/purple and orange, respectively.

The analytical continuation of the self-energy dependence on the real frequencies and evaluated the spectral functions is shown in Figure 3. For a small value of $U = 1$ eV, the spectral function of the electrode states resembles the DOS obtained using DFT. An increase of $U$ up to 2.5 eV leads to a renormalization of the spectral weight and narrowing of the band around the Fermi level. Well-pronounced upper and lower Hubbard bands appear at $+1.8$ eV and $-1.0$ eV, respectively. A further increase of the Coulomb interaction...
The parameter up to 3.5 eV enhances the formation of the quasiparticle peak at the Fermi level and the upper and lower Hubbard bands. For $U = 4$ eV, the transition to the semimetallic state close to that of a Mott insulator is accomplished. The behavior of the spectral function obtained using DMFT for Ca$_2$N resembles the results of the one-band Hubbard model with half-filling. The bandwidth of the electrode state is $\approx 2.0 - 2.2$ eV. The value of the Coulomb interaction was varied from 2 to 4 eV, which yielded the ratio between the Coulomb parameter and the bandwidth $U/W$ from 1 to $\approx 2$. The former corresponds to the intermediate correlated metallic regime, and the latter corresponds to the insulating state. The dynamic Coulomb correlations lead to a strong renormalization of the band structure and a shift of the Fermi level. The magnitude of the shift depends on the Coulomb interaction parameter $U$ and the electronic temperature $T = 1/k_B\beta$. We calculated the effective electron mass enhancement $m^*/m = 1 - \frac{\partial^2 \epsilon}{\partial \omega^2}|_{\omega=0}$ for the $U$ values from 2 to 3.5 eV (Table 1). We have estimated the upper bound of the $U$ parameter using a more localized basis of atomic orbitals by the linear response approach$^{27}$ as implemented in VASP and obtained the value of about $\approx 2.78$ eV. The resulting effective $U$ on MLWFs should have a slightly smaller value due to more effective screening. At $U = 2.5$ eV, the $m^*/m$ equals $2.35m_e^*$ which agrees better with the experimental value of $1.9 - 2.5m_e^*$ and the paramagnetic solution with a local instant squared magnetic moment of $0.76\mu_B$ per electrode site.

To analyze the effect of dynamic correlations on the Ca$_2$N band structure and compare it with the experimental ARPES data,$^7$ we evaluated the energy dispersion along H-A-H and K-G-K directions of the Brillouin zone (Figure 4). A comparison of DFT bands and the ARPES data obtained using DMFT leads to a conclusion that accounting for the dynamic Coulomb correlations between the confined electrons results in smearing and shift of the electrode band down relative to the Fermi level along the A-H direction and up along the K-G direction, whereas the p-N bands are shifted up. The ARPES spectra calculated within DFT+DMFT successfully reproduce the character of the band dispersion near the Fermi level and agree with an experimental intensity map$^7$ better than a simple shift up of the whole band structure obtained using DFT at 0.19 eV as has been proposed in ref$^{27}$.

We started the study of the magnetic properties of Ca$_2$N with the analysis of the behavior of the local spin−spin correlation function $(S_i(\tau)S_0(0))$ on the imaginary-time axis that characterizes the lifetime of the local moment (here $S_i = \sum_{\sigma\sigma'}\epsilon_{\sigma_i\sigma'}\epsilon_{\sigma'_i}\sigma_\alpha\sigma_\alpha'$ and $\sigma^c$ and $\sigma^d$ are the electron creation and destruction operators at orbital $i$, and spin projection $\sigma^c$, $\sigma^d$ are the Pauli matrices$^{30,42}$). If the magnetic moments are localized, this correlator which is an average of the product of expectation values of local magnetic moments at different times is constant: $(S_i(\tau)S_0(0)) \approx S^2$. Such a behavior was observed for $U = 4$ eV (Figure 5): this function is almost zero, which is typical for strongly correlated compounds with highly localized electronic states. On the other hand, the imaginary time dependence of this correlation function at small values of $U$ indicates the delocalization of spin moments, which is the Fermi liquid regime. In the case of itinerant magnetism or strong fluctuations, the lifetime of an electron in a particular

<table>
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<td>1.74</td>
<td>2.35</td>
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Figure 2. Imaginary part of the self-energy as a function of Matsubara frequencies at $\beta = 30$ eV$^{-1}$ for different values of Coulomb parameter $U$ and corresponding Green’s functions in the inset.

Figure 3. Spectral functions obtained using DFT (dashed lines) and DFT+DMFT (solid lines) for $\beta = 30$ eV$^{-1}$ and $U = 2.5$ eV resolved for the electrode (red) and p-N (black) states. The spectral functions of the electrode states obtained using DFT and DMFT for different values of $U$ are shown in the inset. Zero corresponds to the Fermi energy.

Table 1. Effective Electron Mass Enhancement $m^*/m$ and the Fermi Level Shift Relative to DFT Value Obtained Using DMFT at $\beta = 30$ eV$^{-1}$. The Experimentally Determined Electron Mass Enhancement is 1.9−2.5.$^7$

Figure 4. ARPES in H$_2$-A-H$_2$ (corresponds to H-A-H in the hexagonal unit cell) and S$_0$-S$_0$ (K-G-K in the hexagonal unit cell) directions obtained in DMFT calculations at $\beta = 60$ eV$^{-1}$ with $U = 2.5$ eV. Band structure from the DFT calculations is shown by the solid red lines.
state is infinitesimal or the magnitude of the magnetic moment changes rapidly from maximal value to 0 for sufficiently large time intervals. The correlator observed for $U = 1$ eV drops rapidly, which speaks in favor of the weak Coulomb correlations. On the other hand, the square of the magnitude of fluctuating moment decreases with decreasing of $U$ values: for $\beta = 30$ eV$^{-1}$ ($m^s_\beta$) = 0.91 $\mu_B$, 0.75 $\mu_B$, and 0.60 $\mu_B$ for $U$ = 4, 2.5, and 1.0 eV, correspondingly. One can see that the magnitude of the magnetic moment does not drop to zero even for $U = 1$ eV which could be explained as a transition from local magnetism toward band magnetism, that is, the electron delocalization and appearance of Stoner instability. The curve of $\langle S_\sigma(\tau)S_\sigma(0) \rangle$ for $U = 2.5$ eV, having the closest agreement with the experimental mass enhancement, corresponds to an intermediate correlation strength. The temperature dependence of this correlator can be then used as the measure of the localization, for example in the Fermi liquid regime $\langle S_\sigma(\tau)S_\sigma(0) \rangle \sim T/\sin(\tau \pi T)$ for the $\tau$ values that are far enough from 0 and $\beta$. $\langle S_\sigma(\beta/2)S_\sigma(0) \rangle$ is a linear function of $T$ for $U = 1$ eV, which indicates the Fermi liquid regime, that is, the delocalization (Figure 5 inset). By contrast, for $U = 4$ eV this correlator is temperature-independent, which is expected for a system with localized electrons when the magnitude of the magnetic moments is almost frozen at any temperature. For $U = 2.5$ eV, the curve of this correlator lies between those for $U = 1$ and 4 eV, which indicates an intermediate regime with partially localized electrons that is closer to the Fermi liquid at high temperatures.

The local spin susceptibility was calculated as $\chi_{loc} = g_s^2/3 \int_0^\beta d \tau \langle S(\tau)S(0) \rangle$, where $g_s = 2$ is the electron-spin g-factor and $S$ is the spin operator. In contrast to the uniform susceptibility, the local spin susceptibility is evaluated within the nonspin-polarized calculations. The behavior of this quantity for different $U$ values repeats the temperature dependence of $\langle S_\sigma(\beta/2)S_\sigma(0) \rangle$, which strengthens the inference that partially localized and relatively large magnetic moments are present in the interstitial sites for $U = 2.5$ eV (Figure 6 inset).

The correlation function $\langle S_\sigma(\tau)S_\sigma(0) \rangle$ calculated at $U = 2.5$ eV for different values of $\beta$ (Figure 6) shows a similar increase in the localization degree with the increasing temperature: for $\beta = 90$ eV$^{-1}$ (129 K) its curve reminds the one at $U = 1$ eV, whereas for $\beta = 10$ eV$^{-1}$ (1160 K) its behavior is close to the case at $U = 4$ eV. This result is surprising because it contradicts the expectations that temperature should work against the localization. The explanation of this behavior may be found in the specific band structure of the electrode state. A comparison of the DOSes obtained using DMFT for different values of $U$ (Figure 3) shows that the Coulomb correlation leads to a narrowing of the broad DFT band, which should increase the Stoner instability and make a ferromagnetic solution with the band magnetism more preferable. An increase in the temperature acts oppositely, smoothing a sharp quasiparticle peak at the Fermi level, which results in a Stoner instability decrease and a higher localization of the electrode state.

This ambivalent character can be traced in the temperature dependence of the uniform magnetic susceptibility $\chi(T) = m(T)/H$, where $m(T) = \sum (n_i^+ - n_i^-)$ is the magnetization (Figure 7) and $n_i^{(\uparrow)}$ are the occupancies of $i$-orbital with spin-up (spin-down), calculated using DMFT for $U = 1$, 2.5, and 4 eV by applying a small external magnetic field to the Hamiltonian and measuring the magnetization. The uniform susceptibility strictly follows the Curie–Weiss law for $U = 4$ eV, with an estimated Curie–Weiss temperature $\Theta \sim -1700$ K, which indicates a substantial antiferromagnetic (AFM) exchange interaction and localized magnetic moments. The
dependence obtained for \( U = 2.5 \text{ eV} \) has the same behavior in the high-temperature region, but it exhibits a rapid drop below 500 K and a plateau up to 1200 K. The localization degree at \( U = 2.5 \text{ eV} \) is low (Figure 3); we do not imply the presence of any long-range magnetic order, only the AFM fluctuations. The uniform magnetic susceptibility obtained for \( U = 1 \text{ eV} \) has a similar drop at low temperatures but is almost constant in the high-temperature region. The shape of the curves may indicate the existence of the band magnetism with a Stoner-type instability recently predicted for several low-dimensional electrides\(^{20}\) where the magnetic moment and spin density are mainly derived from the interstitial anionic electrons. However, this result means that the magnetism of the electride states in Ca\(_2\)N cannot be described as a conventional band magnetism using the Stoner theory or explained by localized electrons, and a theory combining these two approaches is needed. A similar model has been proposed earlier to describe the magnetism in FeS under pressure.\(^{20}\)

**CONCLUSION**

We demonstrated that Coulomb interactions between the electrons confined in two-dimensional cavities are an essential part of the physics that defines the spectral and magnetic properties of layered electrode Ca\(_2\)N. The electronic correlations of the layered anionic electrons lead to an increase in the effective electron mass (2.35\(m_e\)) and to a renormalization and shift of the energy bands near the Fermi level, which agrees with the experimental observations.\(^{7,27}\) The local spin susceptibility calculations indicate the existence of nonzero local moments in the electrode states. Due to the correlations, the temperature dependence of the uniform magnetic susceptibility revealed a complex behavior of the magnetic subsystem in which the Stoner-type ferromagnetic instability prevails at low temperatures, and an increase in temperature leads to growing localization of the moments and a strengthening of the antiferromagnetic interaction. We suggest that the observed specific traits of Ca\(_2\)N electronic structure and magnetism are expected to be inherent in other two-dimensional electrides.

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