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Band Gap Variation in Prussian Blue via Cation-Induced Structural Distortion

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The charge-transfer band gap of the iron cyanide framework material Prussian Blue and its dependence on the type and location of the charge-compensating interstitial cations (K^+ , Rb^+ , Cs^+) are investigated via periodic density functional (DF) calculations. The calculated variation in the band gap magnitude with respect to cation type confirms recent experimental results on cation-induced spectral shifts. The role of both the cation interaction with the framework and the cation-induced lattice expansion are examined with respect to their influence on the band gap. The gap magnitude is related to the cation type but is found to be more strongly affected by cation-induced lattice distortion as the cation passes through the material. Our results support the possibility of engineering the electronic structure of Prussian Blue type materials through guest-induced host-framework distortion.

1. Introduction

Prussian Blue (PB) is a prototypical mixed valence material comprised of iron metal centers linked via cyanide bridges forming a cubic crystalline framework.¹ The iron centers exist in either a low- or high-spin configuration depending on whether they reside on the carbon or nitrogen side of the C–N bridges² and interstitial cations ensure the charge neutrality of the unit cell. The PB framework is sufficiently open to allow a range of small hydrated ions (K^+ , Rb^+ , Cs^+) to permeate into the structure, which may be interchanged via electrochemical means.³ The favorable ion exchange properties of PB have led to numerous studies into its use in “nanosieving” of cations,⁶ sensors,⁷ battery components,^{8–10} and radioactive waste sequestration.^{4,5} Recently much effort has further focused on the fabrication of PB at the nanoscale (e.g., nanowires,¹¹ nanotubes,¹² nanoparticles,¹³ nanofilms¹⁴) often with a view to improving its desirable application properties.

Although in itself PB is structurally interesting as a host system for guest cations, additionally the PB framework is also electronically rich. Between each cyanide-bridged Fe^{II} – Fe^{III} pair in the PB framework a charge-transfer (CT) ground state defines the material's band gap. The gap magnitude is such that it typically absorbs light in the red end of the spectrum range leading to the material's characteristic blue color. This intrinsic link between electronic/magnetic and optical properties has inspired the synthesis of a range of new PB-analogue materials (differing in type of metal center, and/or bridging unit) with potential electro-optical device applications.^{15–19}

For a fixed choice of metal center and bridging ligand the structural properties of PB and its analogues can be influenced

by changes in stoichiometry, type of interstitial cations, and incorporation of water molecules.^{1,20–22} Recently it has further been experimentally demonstrated that changing the cation also alters the electronic structure of PB, whereby the band gap is also found to vary with cation type.²³ A similar cation-induced band gap change seems also to occur in other PB analogues²⁴ suggestive of a more general phenomena. For PB it has been suggested that a stronger interaction between the interstitial cations and the framework results in a greater stabilization of the CT ground state between Fe centers, and therefore a larger band gap.²⁵ In this study, we investigate this claim through detailed electronic structure calculations in which we track the total energy, band gap, and structural change of the PB system while passing a series of cations (K^+ , Rb^+ , Cs^+) through its open porous framework.

Our calculations confirm the observed electronic band gap variation with cation type²⁵ but also point to an indirect lattice expansion effect rather than solely a direct cyanide–cation interaction induced CT state stabilization. Furthermore, noting the strong interest in pure PB for ion-conducting solid-state electrode applications^{8–10} our study also gives estimates for the energetic barriers for cation transport through the PB framework.

2. Computational Method

All of the presented calculations were performed by using the pseudopotential plane-wave method for solving Kohn–Sham equations as implemented in the Dacapo code included in the CAMPOS package.²⁶ As in our previous studies, we used the Perdew and Wang-generalized gradient approximation (PW91) functional²⁷ and the mixed pseudopotential technique.^{28,29} This methodology allows us to simultaneously capture the mixed-valence electronic state and the accurate optimal structure of PB with reasonably low computational effort, as verified by our previous calculations on PB and its immediate derivative

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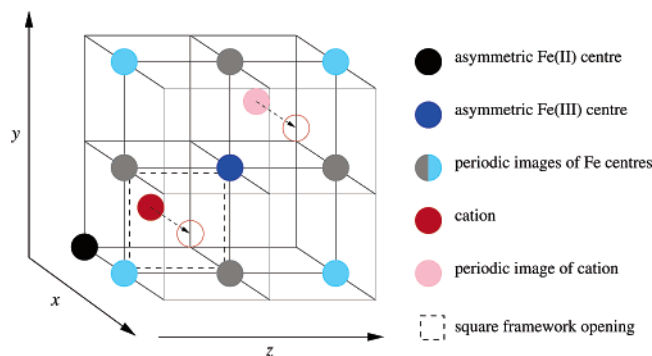


Figure 1. Prussian Blue structure as used for ion mobility calculations. Cyanide ligands and atoms outside the framework crossing plane have been omitted for clarity reasons.

compounds.²⁸ All calculations were done in spin polarized regime with no constraints on the total magnetic moment of the modeled unit cell. To facilitate rapid convergence, a finite electron smearing was used with 0.2 eV smearing for structural optimization, and 0.01 eV for the calculation of electronic structure.

The unit cell parameters were obtained by fitting the quadratic function to the total unit cell energy calculated at several cell geometries, and finding the minimum of the fit. Thanks to the fact that the unit cell is face centered cubic, there is only a single cell parameter that needs to be varied. To minimize the interference of the basis set variability, the calculations were done at a relatively high kinetic energy cutoff of 600 eV. For optimization of the unit cell, all the calculations were performed at Γ -point only. Later, the atomic positions were further refined by performing geometry optimization with a fixed unit cell parameter, using $4 \times 4 \times 4$ Monkhorst–Pack k -point sampling.³⁰

For assessing the variation in the PB system energy, structure, and band gap with cation motion we employed the same computational parameters and fixed the cation movement to within a plane parallel to the square openings in the metal–cyanide framework (i.e., the apertures delimited by four iron center “vertices” and four cyanide “edges”). By setting the constraint plane at different distances from the square opening, we can scan the total energy profile corresponding to the movement of the cation through the opening, and back to its original position at the center of an adjoining framework cage; see Figure 1. Because of the periodicity of the system, the energy barrier obtained in such a calculation is likely to be an upper limit of the real energy barrier for the cation migration because the model system involves all interstitial cations moving in concerted manner through the framework at the same time. Specifically, there are always two cations passing on both sides of each Fe center at once (see Figure 1). This results in immobilization of this central Fe ion, which partially limits the framework flexibility and thus potentially increases the barrier height. In all barrier calculations, the interstitial cation was limited only in its x -coordinate (taken to be perpendicular to the plane of the opening) movement, and the structure was fully relaxed. In all calculations, the y - and z -coordinates of the cation proved to be unchanged, with the lowest energy path between two equilibrium positions being a straight line through the square framework openings.

3. Results

As seen in Table 1, the lattice constants for PB containing K^+ , Rb^+ , and Cs^+ cations follow the expected trend of enlarging

TABLE 1: Calculated Lattice Constants and Band Gaps of Prussian Blue with Different Interstitial Cations, as Well as Ionic Radii of Cations²⁵ for Reference

| cation | ionic radius (\AA) | lattice constant (\AA) | band gap (eV) |
|---------------------------------|-------------------------------|-----------------------------------|---------------|
| K^+ | 1.38 | 10.13 | 1.151 |
| K^+ (a_{Cs}) ^a | 1.38 | 10.20 | 1.082 |
| Rb^+ | 1.52 | 10.19 | 1.083 |
| Cs^+ | 1.67 | 10.20 | 1.077 |

^a Model system; see the description toward the end of the Results section.

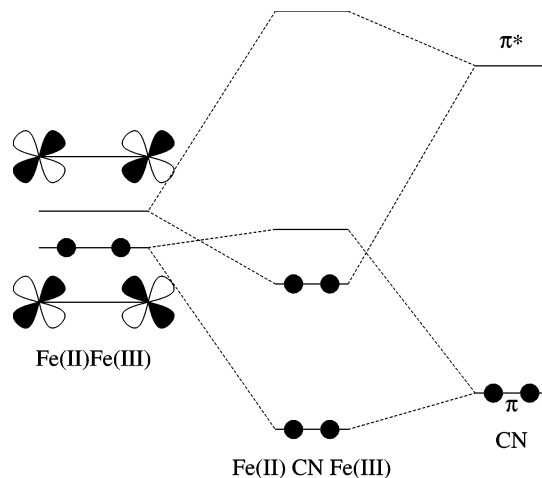


Figure 2. Schematic orbital interaction of the Fe^{II} –CN– Fe^{III} system (see also ref 31 for a more detailed description).

the unit cell with respectively larger interstitial cations. The enlargement of the unit cell is of course restricted by the limited flexibility of the iron–cyanide framework, and it is found to be an order of magnitude smaller than the increase in ionic radii. The increase in the lattice constant is found to be almost solely due to changes in the Fe^{II} –C and Fe^{III} –N ligand–metal linkages, with the cyanide anion geometry virtually unchanged.

Variation in the distance between neighboring Fe centers with respect to the interlinking cyanide ligands inevitably leads to changes in effective exchange interaction between those two Fe centers. With growing cyanide–iron distance, the corresponding change in the overlap between the unoccupied π^* orbital on the cyanide group and the 3d orbitals of the Fe centers influences the overall electronic structure of the material.³¹ In a relatively small range of deformations, the lowering of the aforementioned overlap will result in a pushing of the energy of the d – π^* – d orbital upward toward the energy of the unperturbed π^* state (Figure 2). The expected result of such a change is lowering of the band gap of PB.

The results of the calculations (Table 1) indeed confirm this orbital-overlap picture showing that along with the cation-induced lengthening of the lattice constant, the calculated band gap of the investigated PB materials decreases slightly. This result is also qualitatively consistent with experimentally measured changes in the CT absorption band of PB compounds. The reported broad CT absorption peaks are located at 686, 691, and 703 nm for K^+ , Rb^+ , and Cs^+ , respectively.^{23,25} It is important to note here that although the calculated trend is in agreement with experiment, DF calculations are known to substantially underestimate band gap magnitudes and therefore no quantitative comparison can be made.

It has been suggested by Rosseinsky et al. that the observed cation-induced changes in the band gap of PB are directly caused by the cation–framework interaction strength^{23,25} rather than, as we suggest, the changes in cell parameter due to the lattice

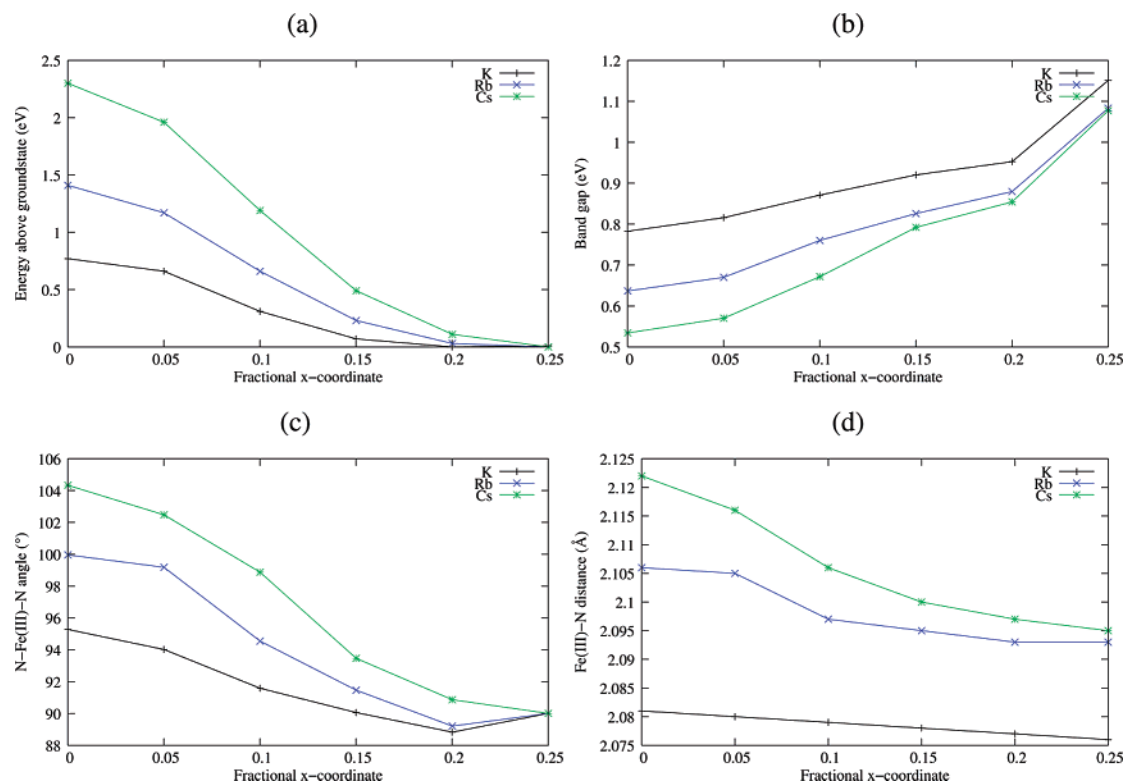


Figure 3. Changes in (a) energies, (b) band gaps, (c) N–Fe^{III}–N angle, and (d) Fe^{III}–N distance when passing an interstitial cation (K⁺, Rb⁺, Cs⁺) through the opening in the iron–cyanide framework. Energies are given with respect to the ground state, in which each cation resides at (1/4, 1/4, 1/4) fractional coordinates.

accommodating cations of variable size. It has been argued that the stronger interaction between interstitial cation and the framework causes a greater stabilization of the CT ground state, and therefore a larger band gap.

In a periodic DF approach we cannot simply remove all the cations from the material to directly calculate their absolute interaction energy with the PB framework due to the instability of the remaining charged infinite system. However, by explicitly moving a cation through the material we can directly investigate the variation in total system energy (which incorporates cation–framework interaction), structure, and band gap for different cation types. The energy change and band gap along a path through an internal opening in the PB material (see Figure 1) for three cations (K⁺, Rb⁺, Cs⁺), giving the respective cation transport barriers, are presented in Figure 3, parts a and b. As can be clearly seen, the magnitude of the total energy variation increases with increasing cation size. These energies are relative system energies with respect to the respective cation-containing PB material with the cation at the center of a cage, and thus do not necessarily represent a similar trend in absolute interaction cation–framework energies. Furthermore, the total energy variation also includes contributions from the energy change due to the cation-induced distortion of the PB crystal, which even for each respective reference state is different. The increasing range of variation in the total energy for increasing cation size does, however, tend to suggest that the larger cations interact more strongly with the PB framework, which is apparently contrary to the trend put forward in the aforementioned study^{23,25} in which the larger cations interact with the framework to a lesser extent.

The proposed link between band gap and cation–framework interaction^{23,25} is based upon the idea of a stabilizing interaction and thus it would be expected that a more attractive (or less repulsive) cation–framework interaction is more favored for

yielding a correspondingly larger band gap. In this way, although the magnitude of the cation–framework interaction seems to increase with increasing cation size, the strength of any stabilizing interaction would vary in the opposing manner in keeping with the original suggestion. Following the variation in band gap with the passage of each respective cation in Figure 3b we indeed see, as for the reference cation position, that the larger the cation the smaller the resulting band gap. It is, however, interesting to note that the variation in band gap size with respect to cation position is larger than the variation in the gap size with respect to cation type at any one position. This shows that the change in band gap is more sensitive to cation position than cation type (at least for the range of cations examined herein) and points once again to cation-induced changes in the structure of PB rather than only the strength of the cation–framework interaction as an important mechanism for band gap variation.

Examining the changes in framework structure with cation passage, the main mode of geometrical change is found to be the angle at which cyanide ligand is attached to Fe^{III} (Figure 3c). As expected from the relative size of the cations the Cs⁺ cation induces more variation in the N–Fe^{III}–N angle than the Rb⁺ and K⁺ cations. For very small displacements from the central equilibrium position we also observe a small dip in N–Fe^{III}–N angle for both K⁺ and Rb⁺ cations. This means that at small displacements from the center of a cage, the ligands bend toward the cation, which suggests a slightly attractive interaction. At smaller distances between cation and ligand, the latter bends outward, and the interaction between cation and ligand is clearly repulsive (see Figure 4 and Table 2). Although it is difficult to extract from planewave calculations, this increased N–Fe^{III}–N angle along with the associated small increase in Fe^{III}–N distance (see Figure 3d) will reduce the overlap between the cyanide ligand and the Fe^{III} center leading

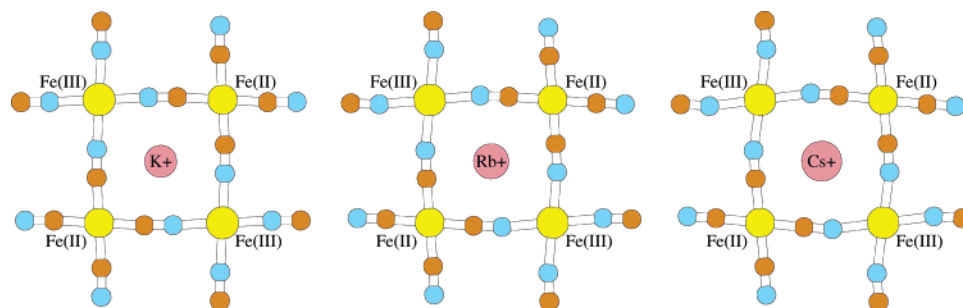


Figure 4. Deformed geometries of PB lattice at the top of the energy barrier. Direct neighboring to Fe^{II} and Fe^{III} are carbon (orange) and nitrogen (light blue) atoms, respectively. Note that the opposing cyanide ligands around the Fe^{II} atom remain axially aligned irrespective of the extent of overall deformation.

TABLE 2: Angles and Distances of the PB Framework for a Cation at the Top of the Energy Transport Barrier^a

| cation | N–Fe ^{III} –N (deg) | C–Fe ^{II} –C (deg) | Fe ^{III} –N (Å) |
|-----------------|------------------------------|-----------------------------|--------------------------|
| K ⁺ | 95.3 | 96.2 | 2.081 |
| Rb ⁺ | 100.0 | 98.6 | 2.106 |
| Cs ⁺ | 104.3 | 101.6 | 2.122 |

^a That is, in the plane of an opening circumscribed by four Fe centers.

to a band gap increase via the mechanism described above. At the top of the energy barrier, a passing cation deforms the framework to its maximal extent. Even here, however, due to the fact that the internal binding strength of the hexacyanide complex anions (i.e., $\text{Fe}^{\text{II}}(\text{CN})_6^{3-}$) is significantly higher than its respective binding with neighboring cations, both Fe^{II} –C and C–N distances remain undisturbed (to within 0.005 Å). The deformation of the hexacyanide anions is comprised mostly of simultaneous axial rotations of opposing ligands in the plane through which the cation passes, and to a much smaller extent of slight dislocation of the atoms a long way from the N–C–Fe^{II}–C–N axis.

In an attempt to discern the relative dependence of the band gap magnitude change on lattice expansion and/or cation–framework interaction stabilization we consider a model system based upon two variants of PB in which the lattice geometry and the cation have been interchanged. Specifically, we take the geometry of the unit cell and atomic coordinates from the fully converged PB containing Cs^+ cations at the center of each cage and substitute these original cations with K^+ . We then calculate the electronic structure of this substituted system with the fixed geometry of the Cs^+ -containing framework. In this way the contribution to the total energy via lattice distortion is fixed and the electronic structure is only affected by the cation–framework interaction. The band gap of this model system is calculated to be 1.082 eV, which is very close to the band gap of the original Cs^+ -containing material. Immediately this result informs us that the observed decrease in band gap is not cation specific and can equally well be achieved with a single cation type and an increase in the unit cell size. Although this appears to suggest a lattice expansion effect is the prime cause of the band gap change it is noted that a small cation (e.g., K^+) in an expanded unit cell will have less of a stabilizing influence on its surrounding C–N groups purely due to the fact that it is further away from them than in the smaller relaxed unit cell. In fact it is quite probable that the effects of CT stabilization and lattice size/distortion are inherently interlinked. For a relatively small cation its physical size allows more space for greater lattice relaxation resulting in reduced unit cell dimensions with an increased π^* –3d overlap and a larger band gap. Furthermore, for such a cation the positive charge is concentrated in a smaller volume making its interaction with nearby anionic species

stronger and thus the stabilization of the CT state is potentially increased also tending to increase the band gap. For larger cations with a more diffuse effective charge distribution the opposite is true and the band gap decreases. In each case the mutual effects from cation-induced CT stabilization and expansion-induced overlap change would be cooperative and jointly give rise to the experimentally observed band gap variation.

4. Conclusions

In this study we have highlighted the important role of internal distortion as a means to vary the electronic structure of PB and its analogues. The ability of species incorporated into PB and its analogues to alter the host's electronic properties via their size and their movement through the material, in addition to their inherent interaction with the framework, may present new perspectives on how to functionalize and utilize such materials for practical applications.

Our calculated results agree qualitatively with the experimentally observed cation-induced band gap variation in PB showing the expected increase in band gap when reducing the size of the cation. We show for (K^+ , Rb^+ , Cs^+) that the cation-induced structural changes to the framework can affect the band gap magnitude in PB more than the variation in cation type. Our indirect structural mechanism should be considered as a major factor in inducing band gap variations in PB perhaps rivaling the importance of the previously proposed electronic mechanism via cation–framework stabilization of the PB CT state. The general result that internal structural change due to incorporated species can significantly alter observable electronic properties of PB materials is of potential technological importance.

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