Ab-initio study of the Coulomb interaction in Nb$_x$Co clusters: Strong on-site versus weak non-local screening

L. Peters,$^1$ E. Şaşoğlu,$^2$ I. Mertig,$^2$ and M. I. Katsnelson$^1$

$^1$Institute for Molecules and Materials, Radboud University Nijmegen, NL-6525 AJ Nijmegen, The Netherlands
$^2$Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, 06120 Halle (Saale) Germany

(Dated: June 23, 2018)

By means of ab-initio calculations in conjunction with the random-phase approximation (RPA) within the full-potential linearized augmented plane wave method we study the screening of the Coulomb interaction in Nb$_x$Co (1 ≤ $x$ ≤ 9) clusters. In addition, these results are compared with pure bcc Nb bulk. We find that for all clusters the onsite Coulomb interaction in RPA is strongly screened whereas the inter-site non-local Coulomb interaction is weakly screened and for some clusters it is unscreened or even anti-screened. This is in strong contrast with pure Nb bulk, where the inter-site Coulomb interaction is almost completely screened. Further, constrained RPA calculations reveal that the contribution of the Co 3d → 3d channel to the total screening of the Co 3d electrons is small. Moreover, we find that both the onsite and inter-site Coulomb interaction parameters decrease in a reasonable approximation linearly with the cluster size and for clusters having more than 20 Nb atoms a transition from 0D to 3D screening is expected to take place.

PACS numbers: 31.15.A-, 31.15.es, 36.40.-c, 36.40.Cg, 73.22.-f,

I. INTRODUCTION

The interest in the field of clusters is growing due to the increasing demand for nano-technology. Besides the relevance for technology, clusters are also fundamentally very interesting. They behave in general very different from their bulk counterpart. Also their electronic and magnetic properties can drastically change by just adding or removing one atom$^{1-4}$ For example, in a recent work on Nb$_2$Co clusters it was demonstrated that Nb$_5$Co and Nb$_7$Co are non-magnetic, while Nb$_4$Co and Nb$_6$Co are strongly magnetic$^5$ The physical origin of this behavior can be traced back to the drastic change of the electronic structure as a function of cluster size.

The study of bimetallic clusters offers a broader playground than for pure clusters. This has resulted in a number of intriguing observations$^5$-10 For example, from an anion photo-electron spectroscopy study on bimetallic Nb$_2$Co clusters, it was observed that for $x = 6$ due to the addition of one Co atom to the Nb$_6$ host, the electronic structure resembles that of a typical bulk semiconductor$^5$ Therefore, this cluster was then proposed as a candidate for semiconductor materials.

From the theoretical side the bond properties and electronic structure of (NbCo)$_x$ clusters has been investigated by means of relativistic density functional theory (DFT)$^{11,12}$ Further, the geometry, stability and electronic properties of neutral and anionic Nb$_2$Co clusters is compared with pure Nb$_2$ clusters within a DFT study$^{13}$ Recently a combined theoretical and experimental investigation has been performed on Nb$_5$Co clusters.$^9$ In this work the geometry is obtained from a comparison of experimentally and theoretically obtained vibrational spectra. With the geometry established the electronic structure is investigated in order to explain the magnetic properties obtained from magnetic deflection experiments.

To our knowledge a systematic assessment of screening and correlation effects in Nb$_2$Co clusters does not exist. This information is crucial in order to obtain a proper fundamental understanding of the system. Namely correlation effects among the electrons inhibit in general an exact solution. Therefore, approximate methods are required in practice. The choice of a suitable approximate method requires knowledge of the effective Coulomb interaction in the system. More precisely, the gradient of the effective Coulomb interaction is of importance$^{13,14}$ A very small gradient means that the effective Coulomb interaction is merely constant, while a very large gradient indicates a purely local effective Coulomb interaction. In the former case a mean-field treatment, i.e. single-particle approach, is probably a good choice, while for the latter it might be the (generalized) Hubbard model.

The aim of the present work is the ab-initio determination of the Coulomb interaction for NbCo to Nb$_7$Co and Nb$_5$Co clusters. Besides being fundamentally interesting, such information is crucial to select an adequate theoretical method for a further investigation of the system. The geometries of Nb$_5$Co to Nb$_7$Co and Nb$_9$Co are well established from a comparison of theoretically and experimentally obtained vibrational spectra$^5$ In addition NbCo and Nb$_2$Co are considered, since the number of isomers is very small. All these clusters are known to be magnetic except Nb$_5$Co and Nb$_7$Co, which are non-magnetic. By employing the full-potential linearized augmented plane wave (FLAPW) method using Wannier functions in conjunction with the random-phase approximation (RPA)$^{15,16,17}$ it is found that in these clusters the onsite Coulomb interaction in RPA is well screened, while the inter-site Coulomb interactions are barely screened. Interestingly for NbCo the inter-site interaction is unscreened, while for Nb$_3$Co even anti-screening occurs. The important consequence being that the screened Coulomb interaction is almost constant throughout the clusters. For completeness these results are compared with pure Nb
bulk for which only the onsite Coulomb interaction is appreciable, while the inter-site Coulomb interactions are almost completely screened. Moreover, our constrained RPA calculations reveal that the Co 3d → 3d channel only plays a minor role in the screening of the onsite Coulomb interaction of the Co 3d electrons. Finally, we find that both the onsite and inter-site Coulomb interaction parameters decrease in a reasonable approximation linearly with the cluster size and for clusters having more than 20 Nb atoms a transition from 0D to 3D screening is expected to take place. The rest of the paper is organized as follows. The method and computational details are presented in Section II. Section III deals with the results and discussion and finally in Section IV we give the conclusions.

II. METHOD AND COMPUTATIONAL DETAILS

In this work the screening of the Coulomb interaction in Nb7Co clusters is calculated by means of the ab-initio random phase approximation (RPA) method. The non-interacting reference system required for this method comes from a preceding DFT calculation. In the following we shortly explain the RPA method and for details we refer to Ref. 8. The screened Coulomb interaction is defined as

\[
W(r, r', \omega) = \int dr''\epsilon^{-1}(r, r'', \omega)v(r'', r'),
\]

where \(\epsilon(r, r'', \omega)\) is the dielectric function and \(v(r'', r')\) is the bare Coulomb interaction potential. Since an exact expression for the dielectric function is not accessible, an approximation is required. In the RPA the dielectric function is approximated by

\[
\epsilon(r, r', \omega) = \delta(r - r') - \int dr''v(r, r'')P(r'', r', \omega),
\]

where the polarization function \(P(r'', r', \omega)\) is given by

\[
P(r, r', \omega) = \sum_{occ\, unocc} \sum_{\sigma, k, m, k', m'} \varphi_{km}(r)\varphi_{km'}^{\sigma}(r)\varphi_{km}(r')\varphi_{km'}^{\sigma}(r')
\times \left[ \frac{1}{\omega - \Delta_{km, k'm'}} - \frac{1}{\omega + \Delta_{km, k'm'}} \right].
\]

Here \(\Delta_{km, k'm'} = \epsilon_{km'}^{\sigma} - \epsilon_{km}^{\sigma} - i\eta\) with \(\epsilon_{km}^{\sigma}\) the single particle Kohn-Sham eigenvalues obtained from DFT and \(\eta\) a positive infinitesimal. Further, the \(\varphi_{km}(r)\) are the single particle Kohn-Sham eigenstates with spin \(\sigma\), wavenumber \(k\) and band index \(m\). The tags \(occ\) and \(unocc\) above the summation symbol indicate that the summation is respectively over occupied and unoccupied states only.

The Eqs. 1, 2, and 3 constitute what is called the RPA of the dynamically screened Coulomb interaction. It is also possible to exclude certain screening contributions from Eq. 3, which is referred to as constrained RPA (cRPA). In this work the screening of the Coulomb interaction for the Co 3d electrons and Nb 4d electrons are investigated. One could for example exclude the screening contribution coming from the Co 3d states to obtain insight in their contribution to the total screening. More details on the method used in this work to exclude certain screening contributions can be found in Ref. 15. Note that recently cRPA has become a very popular method to calculate Coulomb interaction parameters for different classes of materials.

The DFT calculations, providing the input of Eq. 3 are performed with the FLEUR code. This code is based on a FLAPW implementation. All calculations are performed with an exchange-correlation functional in the generalized gradient approximation (GGA) as formulated by Perdew, Burke and Ernzerhof (PBE). Further, all calculations are without spin orbit coupling. As will be demonstrated the effect of screening is on the eV energy scale, while for the Co 3d and Nb 4d electrons the spin orbit coupling strength is at least an order of magnitude smaller. In addition it will be shown (Table I and Fig. 3) that the contribution of these electrons to the screening is small with respect to the other electrons, the Co 4s and Nb 5sp electrons. For such extended states the spin orbit coupling strength is even smaller than for the Co 3d and Nb 4d electrons. Therefore, spin orbit coupling effects are expected to be small for the consideration of effective interactions. Since FLEUR is a k-space code, a supercell approach was employed for the cluster calculations, with a large vacuum between clusters that were repeated in a periodic lattice. In order to prevent the interaction between clusters of different unit cells we performed tests for different unit cell sizes. We found that for a large unit cell of 12 Å dimensions the results are converged to within a few percent. Therefore, this unit cell size is used for our calculations. Further, for the cluster calculations the cutoff for the plane waves is 4.0 Bohr\(^{-1}\), \(k_{\text{cut}} = 8\) and the \(\Gamma\) point is the only \(k\)-point considered. For the calculations of bulk bcc Nb we use the same parameters with a \(20 \times 20 \times 20\) \(k\)-point mesh and experimental lattice parameter of 3.3 Å of the bcc lattice. The ground state geometric and magnetic structure of the Nb7Co to Nb7Co and NbCo clusters is obtained from Ref. 3 (see also Fig. 1). More precisely, the geometries and magnetic structure are obtained from a comparison of calculated and measured vibrational spectra. Structures of NbCo, NbCo and NbCo were not addressed in Ref. 3. Since the structure for NbCo is unclear due to the many possible isomers, we will only address NbCo and NbCo in addition. In order to obtain the ground state geometry of NbCo and NbCo we performed the ATK-DFT calculations using the GGA-PBE exchange-correlation functional and the SG15-Medium combination of norm-conserving pseudopotentials and LCAO basis sets. The total energy and forces have been converged at least to \(10^{-5}\) eV and 0.01 eV/Å, respectively.

The DFT calculations are used as an input for the
the static limit \( \omega \) Here we located at site in practice. Wannier functions, we find that this dependence is negligible due to the spin dependence of the Wannier functions. Formally localized Wannier functions are used to project the \( s \) state and three \( p \) states. Note that although the matrix elements of the Coulomb potential are formally screened (bare) Coulomb interaction of Eq. (1) on, the partially screened onsite Coulomb interaction is usually referred to as Hubbard \( U \)

\[
U_{i\sigma}^{\sigma'} = \sum_{\mathbf{r}, \mathbf{r}'} \langle \mathbf{r} | \mathbf{w}_{j\sigma}^{\sigma'}(\mathbf{r}) W(\mathbf{r}, \mathbf{r}'; \omega) \mathbf{w}_{j\sigma'}^{\sigma}(\mathbf{r}') \rangle (\mathbf{r}).
\]

(4)

Here \( \mathbf{w}_{j\sigma}^{\sigma}(\mathbf{r}) \) is a maximally localized Wannier function located at site \( i \) and spin \( \sigma \). In this work we only consider the static limit \( (\omega = 0) \). Furthermore, we use Slater parametrization,

\[
U_i = \frac{1}{(2l+1)^2} \sum_{m,m'} U_{i,m,m',m,m'}^{\sigma,\sigma'}(\omega = 0) \quad \text{and} \quad V_{ij} = \frac{1}{(2l+1)^2} \sum_{m,m'} U_{i,m,m',m,m'}^{\sigma,\sigma'}(\omega = 0).
\]

(5)

Here \( U_i \) is the screened (bare) onsite Coulomb interaction at site \( i \) and \( V_{ij} \) the screened (bare) inter-site Coulomb interaction between sites \( i \) and \( j \). Note that although the matrix elements of the Coulomb potential are formally spin-dependent due to the spin dependence of the Wannier functions, we find that this dependence is negligible in practice.

### III. RESULTS AND DISCUSSION

In Fig. 1 the geometry of the NbCo to Nb\(_7\)Co and Nb\(_9\)Co clusters is depicted. The blue spheres correspond to the Nb atoms and the red spheres to the Co atoms. Between brackets the point symmetry group of the cluster is indicated. The blue spheres correspond to the Nb atoms and the red spheres to the Co atoms. Between brackets the point symmetry group of the clusters is indicated. In the following we first address the fully screened (RPA) interaction between sites \( i \) and \( j \). Note that although the matrix elements of the Coulomb potential are formally spin-dependent due to the spin dependence of the Wannier functions, we find that this dependence is negligible in practice.

In Table 1, the bare (fourth column) and fully screened (fifth column) onsite and inter-site average Coulomb interaction parameters for the Co 3\( d \) electrons are presented. As it is seen the bare interaction is constant as function of cluster size, while the partially and fully screened interactions decrease with size. This can be attributed to the increase of screening channels with increasing cluster size rather than the delocalization of the Wannier functions. Note that very similar matrix elements for the onsite bare Coulomb interaction for all clusters reflect the fact that the localization of the Wannier functions does not change with increasing the cluster size. Furthermore, the obtained cRPA and RPA Coulomb matrix elements for the Co 3\( d \) orbitals are very close to each other, which means that the contribution of the Co 3\( d \) channel to the total screening is very small compared to the other screening channels (see Table 1).

In Table 2 and 3 only symmetry average onsite Coulomb interaction matrix elements of the Co 3\( d \) electrons are presented. As it is seen the bare interaction is constant as function of cluster size, while the partially and fully screened interactions decrease with size. This can be attributed to the increase of screening channels with increasing cluster size rather than the delocalization of the Wannier functions. Note that very similar matrix elements for the onsite bare Coulomb interaction for all clusters reflect the fact that the localization of the Wannier functions does not change with increasing the cluster size. Furthermore, the obtained cRPA and RPA Coulomb matrix elements for the Co 3\( d \) orbitals are very close to each other, which means that the contribution of the Co 3\( d \) channel to the total screening is very small compared to the other screening channels (see Table 1).

In Table 2 and 3 only symmetry average onsite Coulomb interaction matrix elements of the Co 3\( d \) electrons are presented. As it is seen the bare interaction is constant as function of cluster size, while the partially and fully screened interactions decrease with size. This can be attributed to the increase of screening channels with increasing cluster size rather than the delocalization of the Wannier functions. Note that very similar matrix elements for the onsite bare Coulomb interaction for all clusters reflect the fact that the localization of the Wannier functions does not change with increasing the cluster size. Furthermore, the obtained cRPA and RPA Coulomb matrix elements for the Co 3\( d \) orbitals are very close to each other, which means that the contribution of the Co 3\( d \) channel to the total screening is very small compared to the other screening channels (see Table 1).

In Table 2 and 3 only symmetry average onsite Coulomb interaction matrix elements of the Co 3\( d \) electrons are presented. As it is seen the bare interaction is constant as function of cluster size, while the partially and fully screened interactions decrease with size. This can be attributed to the increase of screening channels with increasing cluster size rather than the delocalization of the Wannier functions. Note that very similar matrix elements for the onsite bare Coulomb interaction for all clusters reflect the fact that the localization of the Wannier functions does not change with increasing the cluster size. Furthermore, the obtained cRPA and RPA Coulomb matrix elements for the Co 3\( d \) orbitals are very close to each other, which means that the contribution of the Co 3\( d \) channel to the total screening is very small compared to the other screening channels (see Table 1).

In Table 2 and 3 only symmetry average onsite Coulomb interaction matrix elements of the Co 3\( d \) electrons are presented. As it is seen the bare interaction is constant as function of cluster size, while the partially and fully screened interactions decrease with size. This can be attributed to the increase of screening channels with increasing cluster size rather than the delocalization of the Wannier functions. Note that very similar matrix elements for the onsite bare Coulomb interaction for all clusters reflect the fact that the localization of the Wannier functions does not change with increasing the cluster size. Furthermore, the obtained cRPA and RPA Coulomb matrix elements for the Co 3\( d \) orbitals are very close to each other, which means that the contribution of the Co 3\( d \) channel to the total screening is very small compared to the other screening channels (see Table 1).
TABLE 1. The bare, partially screened without the Co 3d \( \rightarrow 3d \) channel (cRPA) and fully screened (RPA) average on-site Coulomb interaction parameters for the Co 3d orbitals of the NbCo-Nb_{3}Co and Nb_{5}Co clusters obtained from ab-initio calculations.

| Cluster | Bare (eV) | cRPA (eV) | RPA (eV) |
|---------|-----------|-----------|----------|
| NbCo    | 22.2      | 7.9       | 7.7      |
| Nb_{2}Co| 22.2      | 5.9       | 5.8      |
| Nb_{3}Co| 22.3      | 5.6       | 5.5      |
| Nb_{4}Co| 22.6      | 5.2       | 5.0      |
| Nb_{5}Co| 22.7      | 4.7       | 4.6      |
| Nb_{6}Co| 22.7      | 4.4       | 4.3      |
| Nb_{7}Co| 22.7      | 4.1       | 4.1      |
| Nb_{9}Co| 22.9      | 3.9       | 3.8      |

Unequivalent interactions are shown. Further, in the first column \( U_{1} \) corresponds to the onsite Coulomb interaction of atom 1 and \( V_{1,2} \) to the inter-site Coulomb interaction between atoms 1 and 2 (see Fig. 1). The second column indicates between what type of atoms this refers and the third column corresponds to the distance in Å between them. From this table it can be seen that besides for the Co 3d electrons also for the Nb 4d electrons the onsite Coulomb interaction is well screened and decreases with cluster size. On the other hand, the inter-site Coulomb interaction is much less screened and is more or less constant as a function of interatomic distance. This appears to be due to a decrease in the screening as a function of increasing interatomic distance. Interestingly for NbCo the inter-site interaction is unscreened, while for Nb_{4}Co there is even anti-screening present between Nb and Co at an interatomic distance of 3.89 Å. Anti-screening means that the screened interaction is larger than the bare interaction. By considering the effective interaction between two point charges in a medium, screening is understood to be due to the response (polarization) of the medium to these charges. Similarly anti-screening occurs when the medium is polarized in such a way to increase the bare interaction between the two point charges. This situation is known to occur only for low dimensional systems such as carbon nanotubes, nanoribbons, wires, molecules and clusters.\(^{13,14}\) From a simplistic point of view the two induced point charges can be considered as giving rise to point-dipoles at the positions of the polarizable atoms that constitute the medium. Each point-dipole produces an electric field and depending on its orientation it either increases or decreases the bare electric field coming from the two point charges. Roughly the point-dipoles in between the two point charges are oriented to increase, anti-screen, the bare interaction, whereas the other surrounding point-dipoles lead to a reduction, screening, of the bare interaction.\(^{13,14}\) Therefore, the occurrence of anti-screening crucially depends on the dimensionality of the system and distance between the induced point charges. More precisely, for low dimensional systems the ratio of the region between the point charges and the rest of the medium is larger.

Anti-screening was also recently found in Fe_{2}O_{y} clusters by means of ab-initio calculations\(^{13,14}\). However, the anti-screening appears to be more pronounced in Fe_{2}O_{y} clusters than in Nb_{3}Co clusters. In order to qualitatively understand this, the microscopic point-dipole model can be used. Within this model the atoms of the system are considered as classical polarizable point-dipoles. These point-dipoles are then allowed to respond to an external perturbation, e.g., induced point charges. From investigations on low-dimensional systems by means of this microscopic point-dipole model, it is well established that anti-screening delicately depends on the geometry and polarizability of the atoms constituting the system.\(^{13,14}\)

However, in general it is demonstrated that the inter-atomic distance at which anti-screening occurs increases with increasing polarizability (see for example Fig. 1.10 of Ref. \(^{14}\)). Further, from for example ab-initio calculations on isolated atoms it is known that the polarizability of Nb is larger than that of Fe, Co and O.\(^{13,14}\) Fe and Co have a similar polarizability, which is again larger than that of O. Based on these observations anti-screening in Nb_{3}Co clusters is expected to occur at larger inter-atomic distances compared to Fe_{2}O_{y} clusters, which explains why anti-screening is more pronounced in the latter.

The discussion above on the difference in anti-screening between Nb_{3}Co and Fe_{2}O_{y} clusters is based on the microscopic point-dipole model. It is however not clear if these clusters can be modeled by a collection of point-dipoles. Therefore, it is instructive to also discuss anti-screening differences based on Eq. (3). It is known that anti-screening only occurs in low-dimensional semiconductors and insulators.\(^{13,14,35,36}\) As mentioned above, the critical distance for the appearance of anti-screening increases with increasing polarizability, which can be traced back to the distribution of the occupied and unoccupied electronic states around the Fermi energy (strictly speaking chemical potential for the clusters). In Fig. 2 we present the density of states for Fe_{2}O_{3} and Nb_{3}Co clusters, which is calculated using the Gaussian method with a broadening parameter of 0.1 eV. The polarizability (see Eq. (3)) is inversely proportional to the energy difference between occupied and unoccupied states, i.e., the smaller the energy difference the larger the polarizability. Indeed, as seen in Fig. 2 the Nb_{3}Co cluster has more states around the chemical potential with respect to the Fe_{2}O_{3} cluster despite similar HOMO-LUMO energy gaps of both clusters. As a consequence, the contribution of the term between square brackets in Eq. (3) is larger for the Nb_{3}Co cluster giving rise to smaller Coulomb matrix elements and absence of anti-screening for inter-site Coulomb interactions. Thus, similar as for the microscopic point-dipole model, a small polarization or equivalently polarizability of the system is required to observe anti-screening at short distances.
TABLE 2. The bare and fully screened (RPA) average Coulomb interaction parameters for the Nb 4d and Co 3d orbitals for the NbCo to Nb$_5$Co obtained from ab-initio calculations. Here $U_1$ corresponds to the onsite Coulomb interaction of atom 1 and $V_{1,2}$ to the inter-site Coulomb interaction between atoms 1 and 2 (see Fig. 1). The second column indicates what type of atoms this refers and the third column corresponds to the distance in Å between them. Note that due the symmetry of some clusters, some Nb atoms are equivalent.

| U/V | Atom | Distance (Å) | Bare (eV) | RPA (eV) |
|-----|------|--------------|-----------|----------|
| $U_1$ | Nb   | 0            | 11.2      | 7.2      |
| $U_2$ | Co   | 0            | 22.2      | 7.7      |
| $V_{1,2}$ | Nb-Co | 1.99         | 7.0       | 7.0      |

| U/V | Atom | Distance (Å) | Bare (eV) | RPA (eV) |
|-----|------|--------------|-----------|----------|
| $U_1$ | Nb   | 0            | 10.0      | 5.2      |
| $U_3$ | Co   | 0            | 22.3      | 5.5      |
| $V_{1,2}$ | Nb-Nb | 2.16         | 6.0       | 4.9      |
| $V_{1,3}$ | Nb-Co | 2.33         | 6.1       | 5.0      |

| U/V | Atom | Distance (Å) | Bare (eV) | RPA (eV) |
|-----|------|--------------|-----------|----------|
| $U_1$ | Nb   | 0            | 10.7      | 5.0      |
| $U_4$ | Co   | 0            | 22.3      | 5.5      |
| $V_{1,2}$ | Nb-Nb | 2.40         | 5.6       | 4.5      |
| $V_{1,4}$ | Nb-Co | 2.47         | 5.7       | 4.6      |

TABLE 3. The same as Table 2 for NbCo, Nb$_5$Co and Nb$_5$Co clusters. Here $U_1$ corresponds to the onsite Coulomb interaction of atom 1 and $V_{1,2}$ to the inter-site Coulomb interaction between atoms 1 and 2 (see Fig. 1 for the geometry of the corresponding clusters).

| U/V | Atom | Distance (Å) | Bare (eV) | RPA (eV) |
|-----|------|--------------|-----------|----------|
| $U_1$ | Nb   | 0            | 11.3      | 4.0      |
| $U_2$ | Nb   | 0            | 11.3      | 4.0      |
| $U_7$ | Co   | 0            | 22.7      | 4.3      |
| $V_{1,2}$ | Nb-Co | 2.33         | 6.2       | 3.5      |
| $V_{1,4}$ | Nb-Nb | 2.53         | 5.5       | 3.5      |
| $V_{1,2}$ | Nb-Nb | 2.73         | 5.2       | 3.4      |
| $V_{1,5}$ | Nb-Nb | 2.88         | 5.0       | 3.4      |
| $V_{2,3}$ | Nb-Nb | 3.78         | 4.0       | 3.3      |
| $V_{2,7}$ | Nb-Co | 3.91         | 3.9       | 3.4      |

| U/V | Atom | Distance (Å) | Bare (eV) | RPA (eV) |
|-----|------|--------------|-----------|----------|
| $U_1$ | Nb   | 0            | 11.3      | 3.9      |
| $U_2$ | Nb   | 0            | 11.2      | 3.9      |
| $U_3$ | Nb   | 0            | 11.2      | 3.9      |
| $U_4$ | Nb   | 0            | 11.3      | 3.9      |
| $U_5$ | Nb   | 0            | 11.4      | 3.9      |
| $U_6$ | Co   | 0            | 22.7      | 4.1      |
| $V_{1,8}$ | Nb-Co | 2.30         | 6.2       | 3.4      |
| $V_{1,8}$ | Nb-Co | 2.43         | 5.9       | 3.3      |
| $V_{1,4}$ | Nb-Nb | 2.46         | 5.6       | 3.4      |
| $V_{1,4}$ | Nb-Nb | 2.53         | 5.5       | 3.4      |
| $V_{1,5}$ | Nb-Nb | 2.54         | 5.5       | 3.3      |
| $V_{2,3}$ | Nb-Nb | 2.56         | 5.4       | 3.3      |
| $V_{2,4}$ | Nb-Nb | 2.83         | 5.0       | 3.3      |
| $V_{1,5}$ | Nb-Nb | 2.85         | 5.0       | 3.3      |
| $V_{1,2}$ | Nb-Nb | 2.86         | 5.0       | 3.3      |
| $V_{1,7}$ | Nb-Nb | 2.90         | 5.0       | 3.3      |
| $V_{1,3}$ | Nb-Nb | 3.15         | 4.6       | 3.3      |
| $V_{3,8}$ | Nb-Co | 3.78         | 4.1       | 3.3      |
| $V_{1,8}$ | Nb-Co | 3.97         | 3.9       | 3.3      |
| $V_{1,6}$ | Nb-Nb | 3.98         | 3.9       | 3.2      |
| $V_{2,5}$ | Nb-Nb | 4.08         | 3.8       | 3.2      |
| $V_{1,5}$ | Nb-Nb | 4.26         | 3.7       | 3.2      |
| $V_{2,8}$ | Nb-Co | 4.88         | 3.4       | 3.3      |

| U/V | Atom | Distance (Å) | Bare (eV) | RPA (eV) |
|-----|------|--------------|-----------|----------|
| $U_1$ | Nb   | 0            | 11.5      | 3.4      |
| $U_2$ | Nb   | 0            | 11.4      | 3.5      |
| $U_3$ | Nb   | 0            | 11.4      | 3.4      |
| $U_{10}$ | Co   | 0            | 22.9      | 3.8      |
| $V_{1,10}$ | Nb-Co | 2.42         | 6.0       | 3.0      |
| $V_{1,7}$ | Nb-Nb | 2.53         | 5.5       | 2.9      |
| $V_{2,3}$ | Nb-Nb | 2.57         | 5.5       | 2.9      |
| $V_{1,4}$ | Nb-Nb | 2.82         | 5.1       | 2.9      |
| $V_{2,10}$ | Nb-Co | 3.94         | 3.9       | 2.9      |
| $V_{1,8}$ | Nb-Nb | 3.99         | 3.9       | 2.9      |
| $V_{2,7}$ | Nb-Nb | 4.05         | 3.8       | 2.8      |
| $V_{1,3}$ | Nb-Nb | 4.11         | 3.8       | 2.8      |
| $V_{1,2}$ | Nb-Nb | 4.22         | 3.7       | 2.8      |
| $V_{3,10}$ | Nb-Co | 4.96         | 3.3       | 2.9      |
A similar discussion holds for all other clusters, for instance the NbCo cluster has a similar molecular energy level distribution around the chemical potential as Fe$_3$O$_4$ (not shown). Then, anti-screening is expected to occur at similar inter-site distances in these clusters. For Fe$_3$O$_4$ this is expected to occur a bit below 3.4 Å (see Table I of Ref. 6), while for NbCo indeed just above 3.0 Å. Further, although Nb$_2$Co and Nb$_3$Co show a similar molecular energy spectrum around the chemical potential as the Fe$_3$O$_6$ cluster, anti-screening is not observed, because the inter-site distances are too small compared to Fe$_3$O$_6$. For Nb$_4$Co and larger clusters the density of molecular energy levels around the chemical potential increases and is quite a bit denser than for the Fe$_3$O$_6$ clusters. Therefore, anti-screening in these clusters is only expected for large inter-site distances. For example, in Nb$_4$Co it occurs at 3.89 Å, while for Nb$_7$Co at an inter-site Nb-Co distance of 4.88 Å the situation is very close to anti-screening.

It is instructive to compare the Nb$_2$Co results with pure Nb bulk. In Table 4 the bare, partially screened (without the Nb 4$d$ → 4$d$ channel), and fully screened onsite and inter-site Coulomb interaction matrix elements of the Nb 4$d$ electrons are presented. From this table it is clear that the inter-site Coulomb interaction in RPA is almost completely screened. This is in contrast with what is observed for the clusters (Table 2 and 3). Further, the fully screened onsite Coulomb interaction is more screened than for the clusters. The important observation for pure Nb bulk is that the effective Coulomb interaction is not constant throughout the system. Instead, it is localized, i.e. short ranged with a large gradient. Further, the contribution of the Nb 4$d$ → 4$d$ channel to the screening can be investigated from Table 4. Both for the onsite and inter-site effective interaction this contribution is small, about 1.8 eV and 0.07 eV (for the nearest-neighbor interaction), compared to the contribution of about 11 eV and 4.9 eV of the other channels. The main screening contribution comes from the 5$s$ states, which are present around the Fermi level.

For the Nb$_2$Co clusters the influence of the Nb 4$d$ → 4$d$ channel can be obtained from an inspection of Fig. 2. Here an average of the partially screened (without the Nb 4$d$ → 4$d$ channel) and fully screened onsite and nearest-neighbor inter-site Coulomb interaction parameters for the Nb 4$d$ orbitals are presented as function of cluster size. The cluster size is indicated by $x$, which represents the number of Nb atoms in the Nb$_x$Co clusters. It appears that the contribution of the Nb 4$d$ → 4$d$ channel to the screening of the onsite and inter-site effective interaction increases with cluster size. For instance for the onsite interaction this contribution is about 0.3 eV for Nb$_2$Co and becomes about 0.9 eV for the Nb$_9$Co cluster. In case of the nearest-neighbour inter-site interaction the contribution for Nb$_2$Co is almost 0 eV and becomes about 0.3 eV for Nb$_9$Co. Compared to the contributions of the other channels (see Table 2 and 3 for the unscreened bare values), it can be concluded that the contribution of the Nb 4$d$ → 4$d$ channel to the screening is small. Namely for the onsite interaction the contribution of the other channels is about 5 eV for Nb$_2$Co and becomes about 8 eV for Nb$_9$Co. In case of the nearest-neighbor inter-site interaction this is about 1 eV for Nb$_2$Co and 2.5 eV for Nb$_9$Co.

It is interesting to obtain insight at what cluster size the behavior of the screened Coulomb interaction becomes bulk like. For this purpose Fig. 3 is used again, where the averaged onsite and nearest-neighbor inter-site screened and partially screened Coulomb interaction parameters between Nb 4$d$ electrons are presented as function of cluster size and compared with the pure Nb bulk values of Table 4 (green dashed and solid lines for the onsite cRPA and RPA interactions, respectively). The blue and red solid (dashed) lines correspond to a linear extrapolation of the Nb$_x$Co cluster data points for which the smallest cluster ($x = 1$) is ignored. From these extrapolations it appears that both the averaged onsite and inter-site screened and partially screened Coulomb interaction depend in a reasonable approximation linearly on

![FIG. 2. Calculated spin-resolved total density of states for Fe$_2$O$_3$ and Nb$_2$Co clusters. The Fermi energy (chemical potential) is set to zero.](image)

| Distance (Å) | Bare (eV) | cRPA (eV) | RPA (eV) |
|-------------|-----------|-----------|----------|
| 0           | 13.81     | 2.62      | 0.83     |
| 2.86        | 5.01      | 0.08      | 0.01     |
| 3.30        | 4.35      | 0.04      | 0.00     |
| 4.67        | 3.11      | 0.01      | 0.00     |
| 5.72        | 2.57      | 0.00      | 0.00     |
FIG. 3. The averaged partially screened without the Nb 4d electrons. Furthermore, in Ref. 12 it is correctly predicted within DFT and experiments. This is confirmed by a comparison of the vibrational spectra obtained within DFT and experiments. The green solid and dashed lines represent respectively the onsite fully screened and partially screened Coulomb interaction for pure Nb bulk.

...the cluster size. At a cluster size of $x = 20$ both the onsite and nearest-neighbor inter-site screened interaction have reached their corresponding bulk values, i.e. 0.83 eV (2.62 eV) and 0.01 eV (0.08 eV), respectively. Therefore, we expect Nb$_x$Co clusters with $x$ larger than 20 to have a bulk like behavior.

Finally, we would like to comment on the strength of the electronic correlations in the Nb$_x$Co clusters and Nb bulk. As shown in Table 2 and 3 the effective Coulomb interaction is more or less constant throughout the clusters. In contrast for Nb bulk it has a strong gradient and is local in nature. Although the effective Coulomb interaction in Nb bulk is mainly local, it should not be considered as a (strongly) correlated material. For this purpose the band width should also be taken into account. The band width is about 7.5 eV, which is much larger than the effective onsite Coulomb interaction of 0.83 eV (see Table 4). Therefore, it should be interpreted as a weakly correlated material and standard DFT is expected to provide a good description of the essential physics. This is confirmed by DFT studies on the elastic properties, band structure and electron-phonon coupling of Nb bulk, which are in good agreement with experiments. Due to the almost constant effective Coulomb interaction in the Nb$_x$Co clusters, it is also expected that DFT should be able to capture the essential physics. This is confirmed by a comparison of the vibrational spectra obtained within DFT and experiments. Furthermore, in Ref. 12 it is correctly predicted within DFT that Nb$_7$Co should be non-magnetic. The wrong prediction of Nb$_5$Co to be magnetic is probably due to the consideration of the wrong geometry (see Ref. 3). Besides providing an explanation for the success of DFT in these clusters, our results are crucial to select an adequate method for future investigations on many-body effects, e.g. quasi-particle life times. For example, intuitively one might expect DFT in combination with the dynamical mean-field theory (DMFT) to be suitable for this purpose, because the Co atom can be interpreted as an impurity in a Nb$_x$ host. Since DMFT only properly treats local correlations, while we have demonstrated non-local correlations to be also important, this is not a justified choice. Therefore, an extended Hubbard-like model or the consideration of the cluster within multiplet ligand-field theory are probably more suitable choices.

In addition we expect, that due to the almost constant effective interaction in the Nb$_x$Co clusters, the observed trends are robust with respect to the choice of the exchange-correlation functional. For example, the local density approximation (LDA) and GGA are expected to perform similar due to the constant interaction, because both methods are derived in the limit of a (nearly) uniform electron gas. As a test we made for all clusters a comparison between the density of states in GGA and LDA. Since they were found to be very similar around the Fermi level, it is indeed expected based on Eq. 3 that our results are robust with respect to the choice of the exchange-correlation functional.

IV. CONCLUSION

We have performed RPA and cRPA calculations to reveal the screening of the Coulomb interaction in Nb$_x$Co (1 ≤ $x$ ≤ 9) clusters and pure Nb bulk. We have found that in both the clusters and the bulk the onsite Coulomb interaction in RPA is well screened. On the other hand the inter-site Coulomb interaction is much less screened in the clusters resulting in an almost constant interaction throughout the clusters. This is in contrast with pure Nb bulk, where the inter-site Coulomb interaction in RPA is almost completely screened. Our cRPA calculations have shown that the contribution of the Co 3d → 3d channel to the total screening process of the onsite Coulomb parameters of the Co 3d electrons is negligible. Further, for the clusters investigated the contribution of the Nb 4d → 4d channel to effective onsite and inter-site Coulomb parameters of the Nb 4d electrons appears to be small compared to that of the total screening contribution. Based on our findings we expect both for the Nb$_x$Co clusters and Nb bulk that correlation effects play a minor role and that standard DFT is able to capture the essential physics. For the clusters this is due to the almost constant effective Coulomb interaction and for the bulk due to the band width being much larger than the essentially local effective Coulomb interaction. Finally, it has been found that both the onsite and inter-site Coulomb interaction parameters decrease in a reasonable approxi-
mation linearly with cluster size and for Nb$_2$Co clusters having more than 20 Nb atoms a transition from 0D to 3D screening is expected to take place.

Acknowledgements

The Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) and SURFsara are acknowledged for the usage of the LISA supercomputer and their support. L.P. and M.I.K. acknowledges a support by European Research Council (ERC) Grant No. 338957. E. S. and I. M. greatly acknowledge the funding provided by the European Union (EFRE).