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Maximum entropy method and multipole analysis of the bonding in sodium and vanadium metals

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Abstract

The nature of bonding and the charge distribution in sodium and vanadium metals have been analysed using the reported x-ray data of these metals. The maximum entropy method (MEM) and multipole analysis have been used. The bonding in these metals has been elucidated and analysed. The mid-bond densities in sodium and vanadium are found to be 0.014 and 0.723 electron \AA^{-3} respectively, giving an indication of the strength of the bonds in these materials. From the multipole analysis, the sodium atom is found to contract more than the vanadium atom.

1. Introduction

The study of bonding in metals is an interesting subject because of the variety of uses of metals. The metals sodium and vanadium have found extensive use in the fields of chemistry, industry, research, etc. Sodium and vanadium are very useful in elemental and also in compound form.

The precise study of the bonding in materials is always useful and interesting, yet no study can reveal the real picture, because no two sets of experimental data are identical. This problem turns out to be enhanced when the model used for the evaluation of electron densities is not completely suitable. Fourier synthesis of electron densities can be of use in picturing the bonding between two atoms, but it suffers from the major disadvantage of series termination error and negative electron densities which prevent a clear understanding of the bonding between atoms, the factor which has been intended to be analysed. The advent of the MEM (maximum entropy method) solves many of these problems. MEM electron densities are always positive, and even with limited number of data, one can determine reliable electron densities resembling true densities. Currently, multipole analysis of the charge densities has been widely used to study crystalline materials [1–5]. The multipole technique of synthesizing the electron density of an atom into core and valence parts yields an accurate picture of the bonding in a crystalline system. In this work, such an analysis has also been carried out using the formalism of Hansen and Coppens [6].

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In our series of research studies on the bonding in materials, we have analysed LiF, NaF, GaAs, CdTe and some oxides [7–10] using the MEM technique and reported x-ray data, and obtained precise information on the bonding in the above materials. The nature of bonding in these materials as analysed is found to be ionic, mixed covalent and ionic, and ‘oxide’ bonding.

In the present study on sodium and vanadium, we have attempted to study the metal bonding in sodium and vanadium using the MEM and multipole techniques. The x-ray structure factor data of sodium has been taken from Field and Medlin [11] and that of vanadium has been taken from Linkoaho [12]. Other relevant details can be found from these papers. Sodium has been chosen for the present study because of its very large thermal vibration [11], and it was felt that it would be of interest to analyse the highly reactive nature of the sodium in terms of the strength of the bonding and also the thermal smearing of the valence region. In order to make a comparison of the results with an element having the same structure, vanadium has been chosen, which has a very low thermal vibration parameter [12]. Other factors, such as the quality of the data, have also been taken into account in selecting these systems. Hansen and Coppens [6] proposed a modified electron density model with the option that allows the refinement of population parameters at various orbital levels where the atomic density is described as a series expansion in real spherical harmonic functions through fourth-order Y_{lm} . According to this model, the charge density in a crystal is written as the superposition of the harmonically vibrating aspherical atomic density distribution convolving with the Gaussian thermal displacement distribution as

$$\rho(r) = \sum_k^{\text{atoms}} \rho_k(\vec{r} - \vec{r}_k - \vec{u}) \otimes t_k(\vec{u}), \quad (1)$$

where $t_k(\vec{u})$ is the Gaussian term and \otimes indicates a convolution. The atomic charge density is then defined as

$$\rho(\vec{r}) = P_c \rho_{\text{core}}(\vec{r}) + P_v \kappa'^3 \rho_{\text{valence}}(\kappa' r) + \sum_{l=0}^4 \kappa''^3 R_l(\kappa'' r) \sum_{m=-l}^l P_{lm} Y_{lm}(\vec{r}/r) \quad (2)$$

where P_c , P_v and P_{lm} are population coefficients. Canonical Hartree–Fock atomic orbitals of the free atoms normalized to one electron can be used for the construction of ρ_{core} and ρ_{valence} , but the valence function is allowed to expand and contract by the adjustment of the variable parameters κ' and κ'' . The effect of the temperature can be distinguished from the convoluted and the deconvoluted form of thermal contribution to the charge density as dynamic and static multipole deformation maps. The deformation density in these maps is characterized by

$$\Delta\rho_{\text{multipole_deformation}}(\vec{r}) = \frac{1}{V} \sum [F(\vec{h})_{\text{multipole}} - F(\vec{h})_{\text{spherical_atom}}] \exp[-2\pi i(\vec{h} \cdot \vec{r})] \quad (3)$$

where $F_{\text{multipole}}$ is the Fourier transform of the multipole charge density with or without the convolution of thermal contribution, where the Fourier components are terminated at the experiment resolution.

2. Data analysis

Both the reported data sets have been analysed using the GSAS [13] program from Los Alamos National Laboratory, USA. The reliability index wR for sodium data is found to be 2.2% after successful refinement of the data. The refined Debye–Waller factor is found to be $B_{\text{Na}} = 7.899(96) \text{ \AA}^2$. This value is very large and comparable with that reported ($B_{\text{Na}} = 7.86 \text{ \AA}^2$ [11]). The difference being only 0.039 \AA^2 . The reliability index for the vanadium refinement is $wR = 1.1\%$ and the Debye–Waller factor is found to be $0.404(24) \text{ \AA}^2$.

Table 1. Parameters from MEM refinements.

System	Prior electron density (electron \AA^{-3})	Resolution (electron \AA^{-1})	λ	C	R (%)	wR (%)	Number of cycles
Na	0.2785	0.067	0.024	1.0	2.157	2.356	1464
V	1.6634	0.047	0.024	1.0	0.392	0.498	236

Table 2. Parameters from multipole refinement.

Parameter	Na	V
P_c	9.941(0.364)	17.876(0.403)
P_v	1.132	4.573
κ'	1.691(0.257)	1.108(0.242)
κ''	1.066(0.187)	1.016(0.693)
B (\AA^2)	8.811(0.713)	0.406(0.048)
R (%)	2.39	0.95
wR (%)	6.08	1.15
GoF	3.24	2.90

This value is also comparable to that reported by Linkoaho [12], i.e., $B_V = 0.37 \text{\AA}^2$, the difference being 0.034\AA^2 .

The reliability indices and the matching of thermal parameters with the corresponding reported values for both the atoms indicate that the quality of the data for the electron density analysis is sufficiently good. The same number of data for both the crystal systems has been utilized for the present analysis in order to make a comparison also of the bonding (only insignificant changes in the density maps and the numerical results have been observed on including all the reflections for sodium).

The MEM analysis was carried out as outlined in our earlier papers (Israel *et al* [7, 8], Saravanan *et al* [9], Kajitani *et al* [10]). The cell was divided into 64^3 pixels. In the case of sodium data, the convergence condition $C = 1.0$ was obtained after 1464 cycles of refinement, and the reliability indices are found to be $R_{\text{MEM}} = 2.157\%$ and $wR_{\text{MEM}} = 2.356\%$. The Lagrange parameter λ used was 0.024 for sodium. For vanadium, convergence was obtained after 236 cycles with R -values $R_{\text{MEM}} = 0.392\%$ and $wR_{\text{MEM}} = 0.498\%$. A value of 0.024 was used for λ . The prior densities assumed for sodium and vanadium were $0.2785 \text{ electron } \text{\AA}^{-3}$ and $1.6634 \text{ electron } \text{\AA}^{-3}$ respectively. The resolution of the map was $0.067 \text{ \AA}/\text{pixel}$ and $0.047 \text{ \AA}/\text{pixel}$ for sodium and vanadium respectively. The analysis of the MEM results is given in the next section. Some important results from the MEM refinements are given in table 1. The results of the multipole analysis are given in table 2.

3. Results and discussion

The MEM electron density maps in the density-rich regions of sodium and vanadium on the (100) plane have been given in figures 1(a) and (b) respectively. The density distribution of sodium and vanadium on the (110) plane has been shown in figures 2(a) and (b) respectively. The density maps of sodium and vanadium show highly resolved electron density contours, suitable for precise analysis. Both systems have a body-centred cubic structure. Hence, in sodium, only the valence electronic contribution of the body-centred atom is seen at the centre

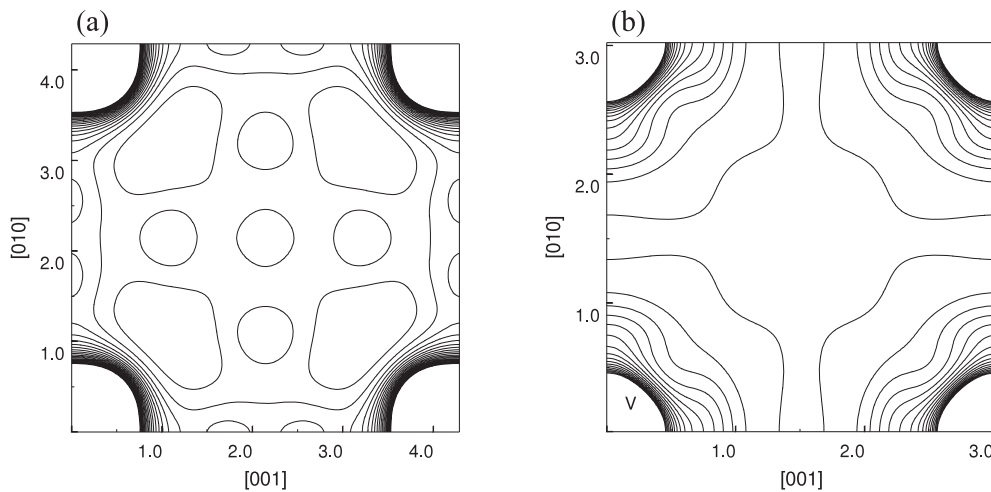


Figure 1. (a) MEM electron density of sodium on the (100) plane. Contour lines are between 0.0 and 1.0 electron \AA^{-3} . The contour interval is 0.05 electron \AA^{-3} . (b) MEM electron density of vanadium on the (100) plane. Contour lines are between 0.02 and 4.5 electron \AA^{-3} . The contour interval is 0.224 electron \AA^{-3} .

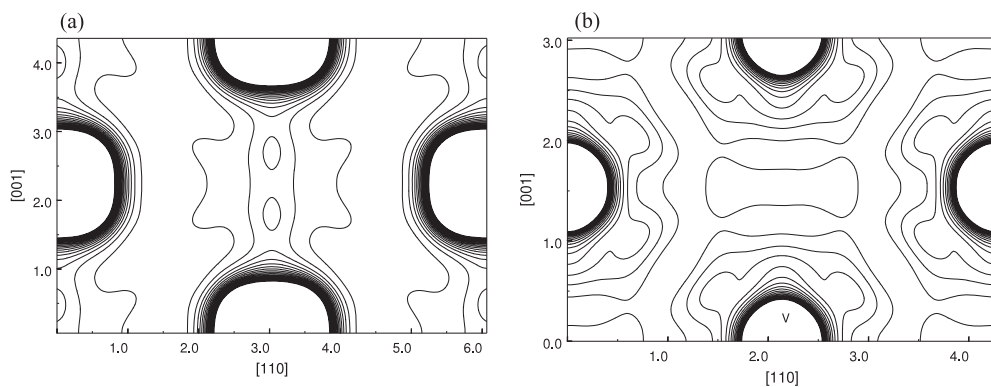


Figure 2. (a) MEM electron density of sodium on the (110) plane. Contour lines are between 0.0 and 1.0 electron \AA^{-3} . The contour interval is 0.05 electron \AA^{-3} . The plane has been shifted half a unit cell along the z -direction. (b) MEM electron density of vanadium on the (110) plane. Contour lines are between 0.04 and 6.0 electron \AA^{-3} . The contour interval is 0.224 electron \AA^{-3} . The plane has been shifted half a unit cell along the z -direction.

of the (100) plane of the cell, as seen from figure 1(a). It also represents the very large thermal vibration of the sodium atom. The corners show that the core regions are perfectly symmetric and spherical. The four voids seen on the (100) plane conform to the crystal system. The conical-shaped contour lines seem to be attracted towards the centre from the corners. This may be due to the fact that core of the centre atom attracts the valence electrons of the eight corner atoms. Since the atomic number of sodium is only 11, this core–valence attraction is very flexible and leads to large smearing of the electrons. Moreover, it should be remembered that the thermal vibration of the sodium atom being very large ($B_{\text{Na}} = 7.899(96) \text{\AA}^2$) makes this electrostatic interaction process highly feasible. The large thermal parameter of sodium

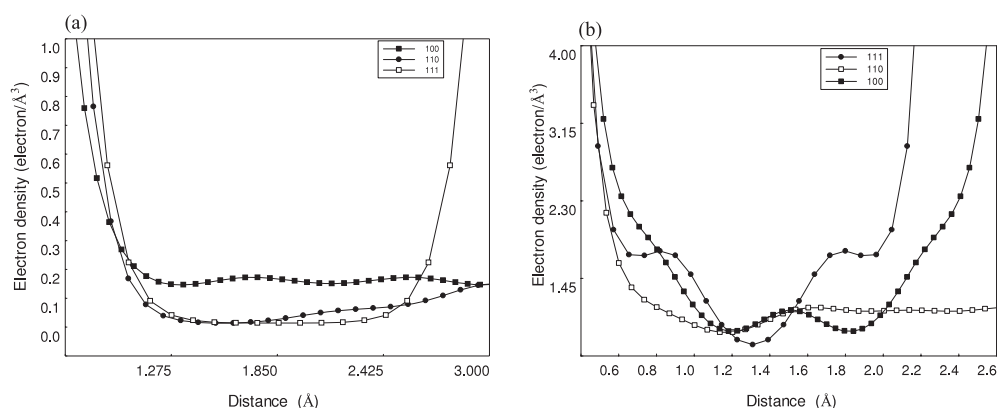


Figure 3. (a) One-dimensional electron density variation of sodium along the [100], [110] and [111] directions. The minimum density is found at a distance of 0.99 Å along the [111] direction. (b) One-dimensional electron density variation of vanadium along the [100], [110] and [111] directions. The minimum density is found at a distance of 1.055 Å along the [111] direction.

and also the smaller atomic number of sodium makes the body-centred sodium atom possible to reveal itself at the face centre.

Figure 1(b) shows the density distribution of vanadium on the (100) plane. The centre of the outer contour lines are bent towards the core of each atom, showing strong attraction of valence electrons by the core, which is due to the large atomic number of vanadium and its smaller thermal vibration parameter. Two humps are seen at the outer contour lines of each of the corner atoms. This may be due to the overlapping of charges between the cores in the bonding direction.

Figures 2(a) and (b) show the densities of sodium and vanadium respectively on the (110) plane (shifted by half the cell distance along the z -direction). Large thermal smearing of the sodium atom is seen (figure 2(a)) as seen from the body-centred atom. The core of one atom attracting the valence of the other atom is also seen. In vanadium also this process is taking place, as seen from figure 2(b).

Figure 3(a) shows the one-dimensional variation of the electron densities of sodium along the three directions, [100], [110] and [111]. The minimum density is found at a distance of 1.732 Å at which the electron density is found to be 0.014 electron Å⁻³. The electron density along the bonding region of the [111] direction is flat, with a low level of density similar to the density along the [110] direction. But, along the [100] direction, the density is slightly higher than that along the other two directions. The large thermal vibration of sodium atom and the smallest interatomic distance along the [100] direction leads to a higher density value along [100]. The interatomic distances are larger along [110] and [111] directions and the lone valence electron of the sodium atom leads to lower densities along these directions. As far as the [100] direction is concerned, the amount of electrons contributing to the bond electron density comes from the corner atom along the [100] direction and the body-centred atom too (due to the large thermal smearing), to contribute to the electron density along the shortest [100] direction.

Figure 3(b) shows the one-dimensional variation of electron density of vanadium along the three crystallographic directions. There is a slight increasing undulation of electron density along the [111] direction. This starts beyond a distance of about 0.7 Å from the centre. The electron density at 1.309 Å is found to be 0.723 electron Å⁻³. This is an indication of the bond

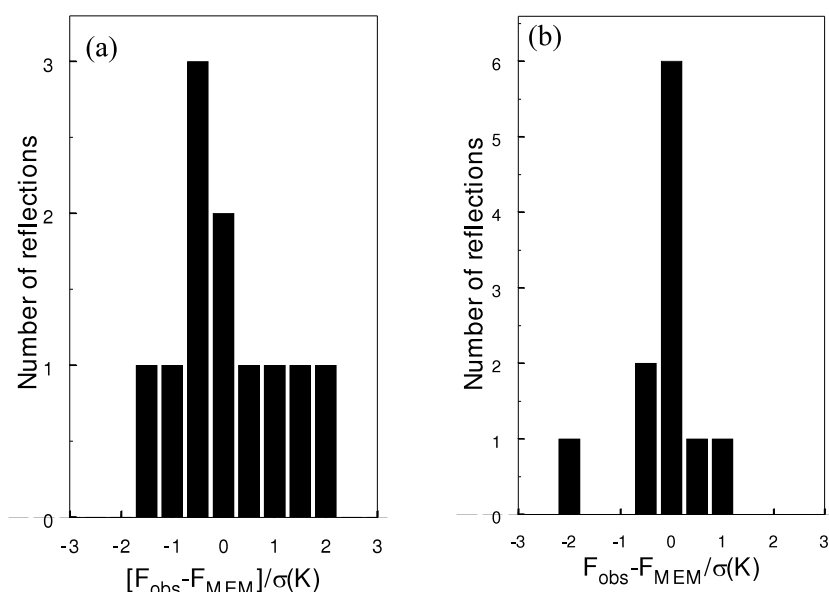


Figure 4. (a) The histogram of number of reflections plotted in the error space of sodium. (b) The histogram of number of reflections plotted in the error space of vanadium.

strength in vanadium compared to that of sodium, which has a density of $0.014 \text{ electron } \text{\AA}^{-3}$. The small ellipses of charge density in the [110] plane as seen from figure 2(b) and the void in figure 2(a) confirm these magnitudes. The reported (Wilkinson, [14]) radii for sodium and vanadium are 1.57 and 1.22 \AA . In the present work, the radii are estimated from the electron densities along the [110] direction, because, along the [100] direction, the atoms are too close to decide the interatomic interactions, and along the [111] direction, the bonding effects are predominant. Thus, the estimated radii are 1.517 and 1.136 \AA respectively for sodium and vanadium, very close to those reported [14].

Figures 4(a) and (b) represent the error analysis of the data used for the present analysis. They conform to the quality of good data sets and justify the use of them for the analysis.

The results of multipole refinement as given in table 2 show the thermal vibration parameters, the multipole parameters and the reliability indices. The large κ' parameter of the valence part of the sodium atom (1 electron) denotes the contraction needed to restrict the lone valence electron to its nearly ideal value of 1. In the present work, the number of core and valence electrons has also been refined in the multipole formalism, for both sodium and vanadium, which leads to very close and reasonable values. For sodium, the core and valence electrons are refined to be $9.94e^-$ and $1.13e^-$, the total being $11.07e^-$, well within the experimental error limits. Only a large κ' parameter will restrict the large thermal vibration of sodium atom to regain this amount of electrons in the valence region. In vanadium, the value of κ' is 1.11, again showing contraction of the atom, but not as much as in sodium. The number of core and valence electrons in vanadium is found to be $17.876e^-$ and $4.573e^-$. There is a deficit of around $0.551e^-$ in vanadium, which actually shows up as a share in the bonding electron and an increase in the mid-bond density. In sodium there is no deficit of total number of electrons leading to a meagre share to the bonding and a decrease in the mid-bond density value. Figures 2(a) and (b) clearly show these features: clear and density-free regions in sodium and charge-accumulated mid-bond regions in vanadium. Our results are based on

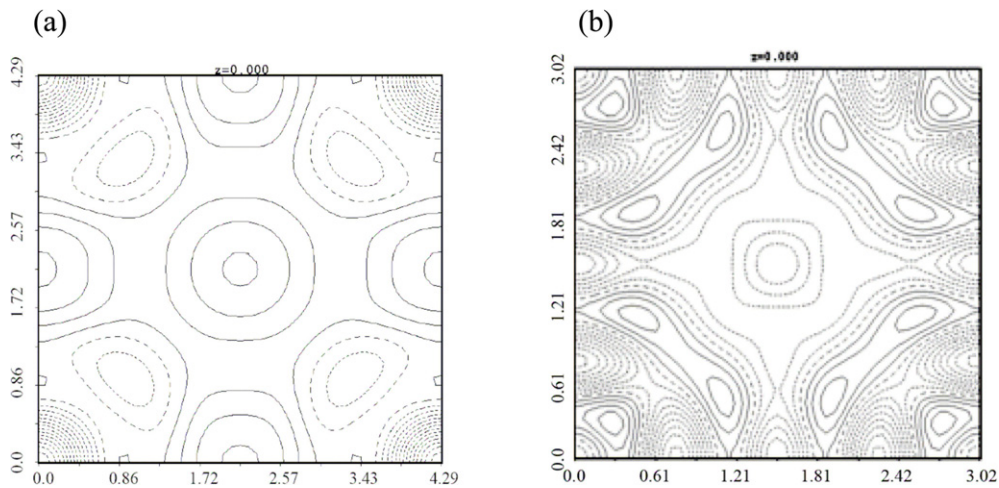


Figure 5. (a) Static multipole deformation map of sodium on the (100) plane. Dotted lines indicate negative electron densities. (b) Static multipole deformation map of vanadium on the (100) plane. Dotted lines indicate negative electron densities.

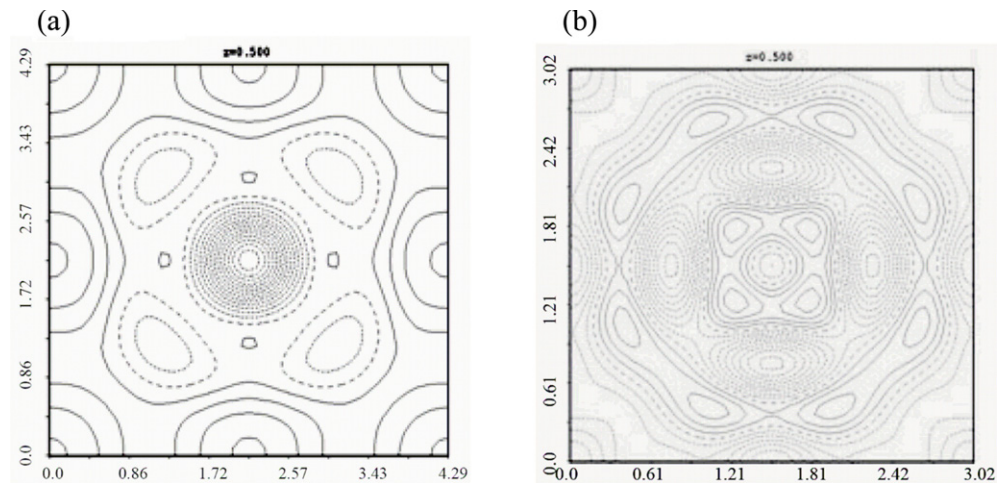


Figure 6. (a) Static multipole deformation map of sodium on the $(\frac{1}{2}00)$ plane. Dotted lines indicate negative electron densities. (b) Static multipole deformation map of vanadium on the $(\frac{1}{2}00)$ plane. Dotted lines indicate negative electron densities.

the limited available information on the structure factors in sodium and vanadium. Thus MEM and multipole results are complementary to each other.

The static multipole deformation maps are shown in figures 5(a) and (b) for sodium and vanadium respectively on the (100) plane and figures 6(a) and (b) on the $(\frac{1}{2}00)$ plane. Figure 5(a) shows positive electron contours on the centre of the (100) plane, edge centres and corners too, though the values of these densities are very small. Still, right from the core, positive densities are seen, showing enhanced thermal vibration of the sodium atom and the contracted spherical core in line with the κ' parameter of sodium. The $(\frac{1}{2}00)$ section (figure 6(a)) also shows the sodium atom with large thermal vibration of the valence region.

Figure 5(b) shows the nullified core and residual valence region (in terms of thermal vibration) of the vanadium atom on the (100) plane. The core is not seen to be as much contracted as in the case of sodium as seen from figure 6(b).

4. Conclusion

An analysis on the simple metals sodium and vanadium has been made in terms of the structural parameters and the electron densities using the best versatile analytical tools available today for the x-ray diffraction data. The large thermal vibrations of the sodium atom and the small thermal vibration of the vanadium atom can be well accounted by the two methods, namely, MEM and multipole. Highly precise electron density maps have been obtained for these two systems which reveal the nature of the metallic bonding. The strength of the bonding in sodium and vanadium has been assessed by the obtained mid-bond densities in these systems (0.014 and 0.723 electron \AA^{-3} respectively). It is believed that the accuracy of the data is very important in studies like the present one.

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