

Intermediate Range Order and Bonding Character in Disordered Network-Forming Systems

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Received March 16, 1998

Revised Manuscript Received October 22, 1998

The neutron structure factor of many disordered network-forming materials exhibits a first sharp diffraction peak (FSDP)^{1–5} at small scattering vectors. This feature is related to the intermediate range order which establishes on length scales substantially larger than nearest neighbor distances. To explain the origin of the FSDP, several interpretations have been invoked, which mostly rely on the presence of super-structural units.^{1,5} The nature of the bonding character in these systems is assumed to be ultimately responsible for the instauration of an intermediate range order. An analysis of a series of network-forming systems supports the view that the FSDP is a signature of directional bonding with a high degree of covalent character.⁶ However, a study of hard-sphere models showed that Coulombic interactions alone are sufficient to give rise to a FSDP.⁷ Therefore, to elucidate the relation between intermediate range order and bonding character, an electronic description which includes both covalent and ionic contributions is highly desirable.

We here address this issue by focusing on liquid GeSe₂, which shows a marked FSDP and which is thought to consist predominantly of tetrahedral subunits.^{8,9} Because the electronegativities of Ge and Se are rather close, the bonding in such systems is assumed to result from a delicate balance of covalent and ionic character. These aspects are accurately accounted for by treating the electronic structure within density functional theory. We consider two distinct energy functionals, which differ by the way the exchange and correlation energy is accounted for. The first functional we considered is a generalized gradient approximation (GGA) which was recently introduced.¹¹ The second is the local density approximation (LDA).¹⁰ A comparison between the structural properties obtained with these two functionals allows us to determine how subtle variations of the electronic structure affect intermediate range order.

The structural data corresponding to the GGA functional are taken from a first-principle molecular dynamics simulation of

liquid GeSe₂ performed previously.¹² Such a simulation is here repeated using the LDA functional but with otherwise identical conditions. In both the GGA and LDA schemes, the electronic structure evolves self-consistently during the molecular dynamics.¹³ Our system consists of a stoichiometric composition of 120 atoms in a periodically repeated cubic cell of side 15.7 Å, corresponding to the experimental density of the liquid. Time averages are taken over periods of 7.5 ps at a temperature of 1000 K.

The neutron-scattering structure factor calculated in the GGA scheme¹² shows excellent agreement with experiment (Figure 1).^{8,9} In particular, the position and the height of the FSDP are accurately reproduced. However, the agreement between the LDA and the experimental structure factor is significantly worse. Important differences are found for small magnitudes of momentum transfer q , and only at large q is the structure factor properly described. The most striking shortcoming of the LDA result is the absence of a FSDP.¹⁴ This demonstrates that intermediate range order is highly sensitive to detailed aspects of the electronic-bonding properties.

To investigate the electronic structure in liquid GeSe₂, we select an instantaneous atomic configuration generated during the molecular dynamics run.¹⁵ For this configuration, we calculate the electronic structure in both the GGA and the LDA schemes. The contour plots of the valence charge densities in the plane of a selected Se–Ge–Se trimer show at first glance similar features for the two functionals (Figure 2). The depletion of the valence charge at the Ge sites and the charge accumulation around the Se atoms result from the ionic character of the bonding. The appearance of lobes pointing along the bond directions are indicative of a covalent contribution to the bonding character. A closer look to the contour plots shows that the charge transfer in the GGA scheme is more pronounced than in the LDA one. This is even more evident from the contour plot of the difference between the charge densities obtained with the two functionals. The spherical nature of the charge distribution in the difference contour plot has important implications. The distinction between the two schemes lies in the way the ionic character is described, with the GGA favoring a higher degree of ionicity. The covalency remains essentially equivalent in the two schemes. Thus, the appearance of a FSDP in the neutron structure factor can unambiguously be ascribed to an increase in the ionic character of the bonds.

To identify the critical features leading to FSDP signatures, we investigate the structural properties of the liquid by calculating the percentage of Ge atoms coordinated by a given number of Se atoms, as a function of the coordination radius (Figure 3). For a coordination radius of 3 Å, corresponding to the first minimum in the Ge–Se pair correlation function, we find that only 50 and 63% of the Ge atoms form tetrahedral units in the LDA and GGA schemes, respectively. Therefore, the picture based on a perfectly ordered tetrahedral network occasionally disrupted to allow for diffusion as found for liquid silica¹⁶ does not provide

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(14) This is at variance with the Harris-functional LDA results obtained in Cobb, M.; Drabold, D. A. *Phys. Rev. B* **1997**, *56*, 3054, where a FSDP is observed in the total structure factor of liquid GeSe₂. This difference should be attributed to (i) a *nonselfconsistent* treatment of the electronic structure, and (ii) the use of a minimal basis set. These approximations may give the Ge–Se bond a different ionic character compared to a converged LDA calculation.

(15) The atomic configuration used in Figure 2 was generated with the GGA scheme. Use of a configuration generated with the LDA scheme does not affect the conclusions which are drawn.

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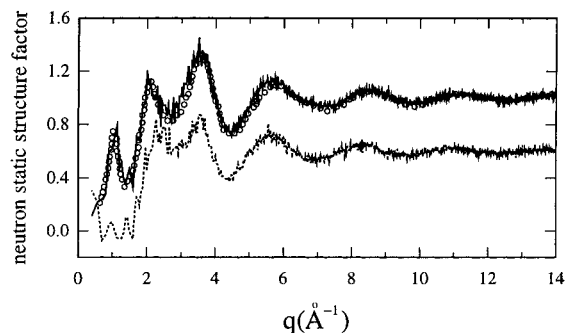


Figure 1. Neutron structure factor $S(q)$ as a function of magnitude of momentum transfer q for liquid GeSe_2 , obtained within GGA (solid line) and LDA (dots), compared to experiment (circles), ref 8. For clarity, the LDA curve is displaced downward by 0.4. We used scattering lengths of $b^{\text{Ge}} = 8.189$ fm and $b^{\text{Se}} = 7.97$ fm.

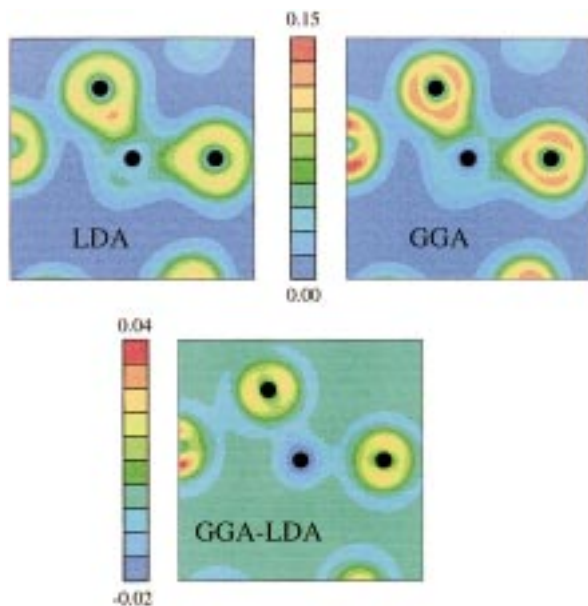


Figure 2. Contour plots of valence electronic charge density for a selected Se-Ge-Se trimer within liquid GeSe_2 in the LDA (upper left) and GGA (upper right). A difference plot (GGA - LDA) is also shown (lower). The scales are in atomic units.

an adequate description. However, it is evident that in the GGA scheme the 4-fold coordination stands out, being the predominant coordination for radii between 2.5 and 3.8 Å. Such a behavior is not observed in the LDA case where the coordination number gradually increases as a function of the coordination radius. This increased chemical order of the GGA configurations is also reflected by the number of homopolar bonds coexisting with the tetrahedral units. In the LDA scheme, we find that 60 and 25% of the Se and Ge atoms, respectively, form homopolar bonds. These values reduce to 39 and 10% when the GGA functional is used. The occurrence of homopolar bonds is consistent with experimental observations.⁹ Hence, an increase of the degree of ionicity is responsible for an enhancement of chemical order in the form of tetrahedral units, which in turn establish an intermediate range order featuring a FSDP.

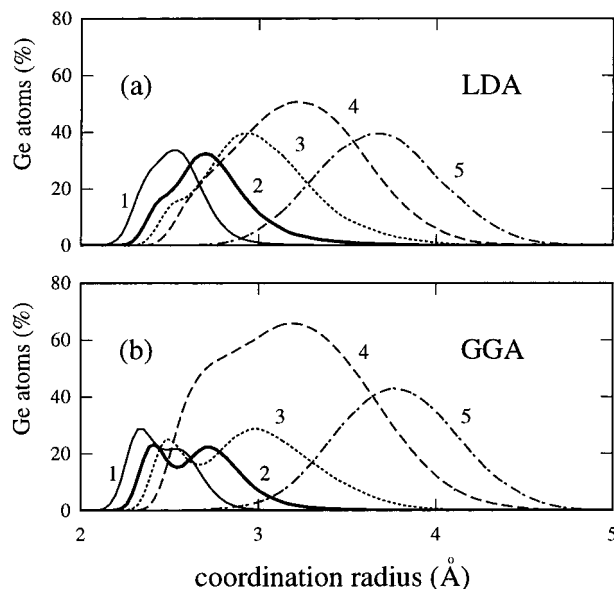


Figure 3. Average Se-coordination of Ge atoms in liquid GeSe_2 as a function of the radius of the coordination sphere in the (a) LDA and (b) GGA. The coordination is defined as the number of nearest neighbors in the coordination sphere.

A detailed analysis of the GGA structure is given in ref 12, where the partial structure factors are compared to experimental results obtained by isotopic substitution in neutron diffraction.⁹ Despite a very good agreement for the short-range structural properties, the distribution of the weight of the FSDP among the partial structure factors shows differences between theory and experiment. However, the good agreement for the total structure factor supports the view that this results from a finer level of detail in the description of the structure.

This work has important implications for the choice of energy functionals in the study of disordered systems. So far, GGA functionals have been recognized to correct several LDA deficiencies. These include binding energies of molecules¹⁷ and solids,¹⁸ energy differences between different bonding configurations¹⁸⁻²⁰, and bond distances in weakly bonded systems.^{21,22} The present study shows that the use of a GGA functional is also crucial to describe structural order in disordered covalent systems.

By accurate first-principles studies of liquid GeSe_2 , we provide evidence for the notion that in the presence of a given degree of covalency, the appearance of a first sharp diffraction peak is conditioned by the presence of a sufficiently strong ionic character. The increased ionicity correlates with an enhanced chemical order via the formation of tetrahedral units.

JA9808447

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