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Principal component analysis on properties of binary and ternary hydrides and a comparison of metal versus metal hydride properties

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ABSTRACT

Principal component analysis (PCA) is used to investigate interrelationship among material properties of hydrides. Property data which consist of ~200 compounds (binary and ternary metal hydrides) were analyzed. A comparative study was carried out among the metal properties with that of their hydrides. The observed decrease or increase of entropy, molar volume and specific heat of hydrides from that of the metals can be attributed to hydrogen bond formation, charge transfer and corresponding change in crystal structure.

1. Introduction

Storage is a challenging issue that cuts across production, delivery and end-use applications of hydrogen as energy carrier. Hydrogen stored in hydrides is safe and has a high hydrogen density. Hydrides are promising materials both as fuel in automobiles and many others such as in rechargeable batteries, fuel cells, refrigerator, heat storage, nuclear industry, sensors, optical switch, and hydrogen purification. The light element hydrides are good candidates for transportation [1]. The transport sector requires not only cheap, safe and reliable way of storing hydrogen but also high storage capacity, fast kinetics and favorable thermodynamics. A practical hydrogen storage candidate, which meets all the mentioned criteria, has yet to be discovered. Main problems of hydrides are weight, volume, cost, safety, efficiency, refueling time, durability, etc. [2]. Therefore, it is important to study their properties to design suitable hydrides for specific applications.

Material informatics is a developing area in material science in which a new knowledge system is built by collecting and classifying information with the help of calculations and databases. If experience and knowledge, captured and preserved in a database format, it helps to investigate new materials efficiently. The abundance of parameters causes difficulties in the interpretation of their relation. Many datum sets can be correlated to define a single material property with the help of a mathematical technique. The main challenge in this field is the difficulty in correlating many properties of different set of materials. Most of the classical analytical methods for finding characteristics of data set are very laborious and time consuming.

Lot of experimental and theoretical work has been done on hydrides in search of a suitable material. A detailed hydride research database is required for proper retrieval of information already available. We collected data from available journal publications and constructed property database (which has to be published soon somewhere else). Data sets in the hydride database can be correlated to define a single material property using available mathematical technique such as principal component analysis (PCA) which is a widely used tool for dimensionality reduction and for visualization of variable patterns. In this work we have considered only binary (of the form MH_x, where $x = 1$, 2 or 3 and M is a metal) and ternary (of the form $A_aB_bH_x$, where a, b and x are integers and A, B are metals) metal hydrides. We have excluded other hydrides due to the presence of large missing data and associated error on analysis. This work investigates correlation among material properties and compares various metal hydride properties with corresponding metallic properties.

2. Data

We have collected properties which include but not limited to specific heat (Cp), entropy (S), molar volume (V) and hydrogen weight percentage (HWt%) of metal hydrides as well as the sum of

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elemental properties of the metals corresponds to each compound and constructed a database. Light metal hydrides (e.g., LiH) have good hydrogen storage capacity (12.6 wt%) but operation temperature (300 °C) is very high while transition metal hydrides (e.g., $LaNi_5H_6$) release H_2 at room temperature (27 °C) but with less storage capacity (<2.5%). In order to understand property interrelationships of hydrides we have carried out PCA by considering the properties such as entropy of metal hydrides (S_{MH}), molar volume of metal hydrides (V_{MH}), sum of specific heat of metals (Cp) in each hydride, specific heat of metal hydrides (Cp_{MH}), sum of entropy of metals (S_M) in each hydride, hydrogen weight percent (HW%) of hydrides and sum of the molar volume of metals (V_M) in each hydride. We have included only these properties in the current study due to the unavailability of enough data on other properties.

3. Method

We have considered property data of both binary and ternary hydrides for the study of their interrelationships. If we have large number of variables and some of which are correlated, we are required to consider only fewer variables that capture maximum variation in the original data set. For this purpose, a better approach is to consider all properties and carry out principal component analysis. PCA can reveal certain characteristics or combinations of the original variables that mostly determine the structure of the data distribution which may not be related to known influencing factors in the data set. PCA is one of the widely used techniques for dimensionality reduction with widespread applications to pattern recognition, data classification, exploratory data analysis, economics, life sciences, chemistry, geology, material science, etc. [3–8]. Due to fascinating interrelationships of material properties, use of PCA analysis has wide application in material science.

The data reduction in PCA is achieved by transforming variables to principal components, which are uncorrelated (orthogonal) and ordered so that the first few retain most of the variation in the total set of original variables with descending importance. If some of the variables in data set are correlated, we need only a minimum number of linear combinations to describe most of the variability in the data set. Correspondingly, for less-correlated data sets, more combinations are necessary. Such linear combinations are called principal components (PC). As an example, if the first three components explain ~90% of the variability among the original data set of 10 variables, the number of variables to be analyzed has been reduced from 10 to 3. In PCA the initial data matrix is represented as the inner product of row/score matrix and column/loading matrix. The row matrix has the dimensionality $r \times n$, where r is the number of observations (i.e., compounds) in the initial data set, and n is the number of principal components. The column matrix has the dimensionality $n \times c$, where c is the number of observable properties (variables) in the initial data set. If we plot a score vector against another score vector, compounds with similar properties will cluster [9–11].

PCA analysis is carried out by forming a matrix with columns as hydride properties and rows corresponds to various hydrides. Based on the matrix diagonalization procedure in SPSS-15 (Statistical Package for Social Sciences), we obtained principal components (eigenvectors) of the matrix. The eigenvectors are termed component loadings and they are used to calculate the component scores. PCA eigenvectors provide information about contribution of each variable to a component. This study help us to correlate variables having common behavior and hence to classify hydrides with respect to their chemical/physical nature.

We have used PCA option for Factor Analysis (FA) in SPSS. FA is solely concerned with correlations among variables. The methodology of FA is very similar to PCA except that unique variability is excluded from the analysis. The output from the SPSS program is not identical to that of generally used PCA analysis. By default it will only extract factors whose eigenvalue is greater than one. If we adjust the number of factors equal to variables we can overcome the difference between PCA and FA. Then the communalities (sum of the common components) are all 1.00 thus all the variability is assumed to be common. In SPSS, factor loadings (component matrix) are eigenvector normalized by the square root of its eigenvalue. If we want the actual PCA we can find the eigenvectors from the loadings by dividing each loading with the square root of the eigenvalue. The PCA derive a small number of linear combinations (PCs) of a set of variables that retain most of the information in the original variables. The projection of variables onto a PC is called scores. Plots of the scores for two or more PCs help us to find graphically the similarities and differences among variables. The distance between points in a score plot shows if they are similar or different [4]. Thus we may be able to find materials with similar properties (corresponds to closer points) which will help us to select new hydrides for particular applications.

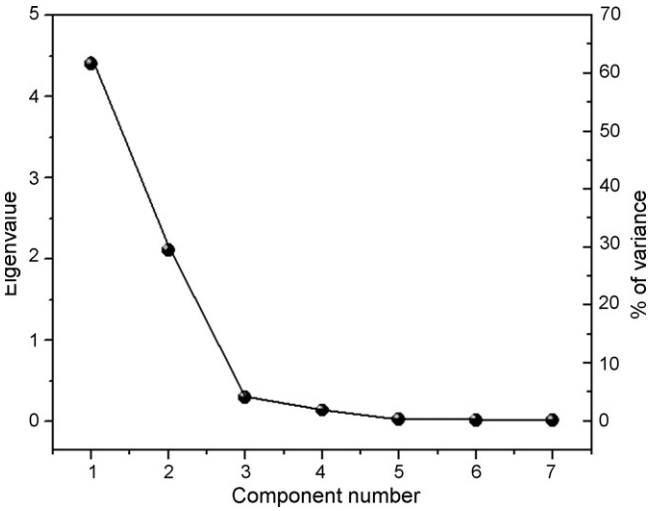

Fig. 1. Eigenvalue and total variance explained by each component obtained from PCA of a set of data with both binary and ternary metal hydrides.

Because of randomly distributed missing data in our dataset we have used pairwise deletion option in PCA to have a reasonable result. To achieve a clear pattern of coefficients, we can rotate PC axes in any direction without changing the relative locations of the points to one another with a change in actual coordinates of the points. The rotated solutions explain the same amount of variance as the original solution [12]. Varimax method of orthogonal rotation is an analytical way for rotation of PC solutions. The varimax rotation maximizes the sum of the variances of the squared coefficients within each eigenvector while the rotated axes remain orthogonal. We have carried out varimax normalized rotation to maximize the values of the loading factors of each compound analyzed.

4. Results and discussion

4.1. Principal component analysis (PCA)

A data set of hydride properties with ~200 compounds is interpreted. We have carried out PCA on a set of data which consists of both binary and ternary hydrides as well as on sets of data which contain just binary or just ternary hydrides. Fig. 1 shows eigenvalues and the variance explained by each principal components (PCs) obtained from the analysis of a set of data with both binary and ternary metal hydrides. Number of factors to be considered for extracting proper information is determined from the screeplot (plot of eigenvalue versus component number) and the percent variance. From the sudden fall of eigenvalues or the loadings of PCs (Fig. 1) it is obvious that the first two PCs (which explains 62.89% and 30.15% variance, respectively) reduced the seven dimensional data set to a two dimensional data set, with an average 6.96%

Table 1
Correlation matrix obtained from PCA of a set of data with both binary and ternary hydrides. Subscript M denotes metal and MH denotes metal hydride. *S*—entropy, Cp—specific heat, *V*—molar volume and HWt%—hydrogen weight percent in each compound.

	V_M	S_M	Cp_M	Cp_{MH}	V_{MH}	HWt%	S_{MH}
V_M	1.000	0.859	0.226	0.049	0.499	−0.482	0.386
S_M	0.859	1.000	0.602	0.352	0.714	−0.398	0.694
Cp_M	0.226	0.602	1.000	0.897	0.855	0.343	0.948
Cp_{MH}	0.049	0.352	0.897	1.000	0.857	0.587	0.899
V_{MH}	0.499	0.714	0.855	0.857	1.000	0.171	0.940
HWt%	−0.482	−0.398	0.343	0.587	0.171	1.000	0.251
S_{MH}	0.386	0.694	0.948	0.899	0.940	0.251	1.000

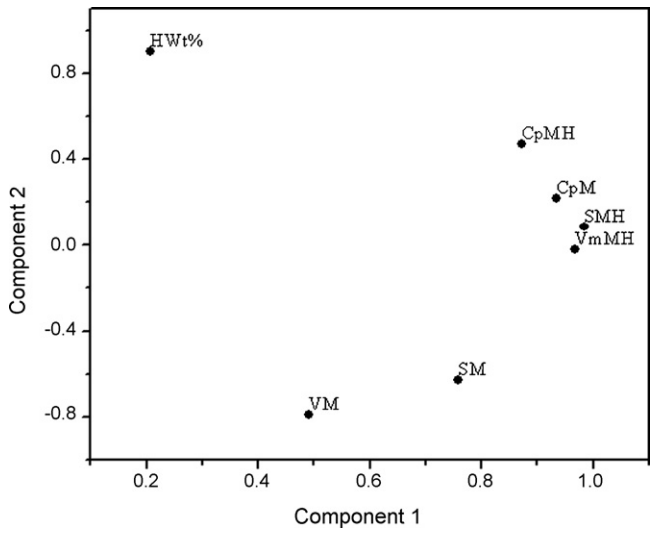

Fig. 2. Component plots for a set of data with both binary and ternary hydrides. Subscript M denotes metal and MH denotes metal hydride. *S*—entropy, Cp—specific heat, *V*—molar volume and HWt%—hydrogen weight percent in each compound.

loss of detail. The correlation matrix for this analysis is given in Table 1. In order to evaluate the correlation between variables, it is important to know the magnitude or strength of the correlation coefficient as well as the significance of the correlation. If the PCA plots show interrelationship among many properties, it is not required to study all the properties of a hydride to determine its overall performance. The analysis shows correlations among Cp_M, Cp_{MH}, S_{MH}, and V_{MH}.

The plot of first two PCs obtained from PCA of a set of data which contain both binary and ternary hydrides is shown in the Fig. 2. The selected properties are found to be confined to PC1-PC2 plane of the component plot which suggests that the first two components explain most of the variability in the data set as predicted from the screeplot. As two PCs cover ~93% of the variance, plot of first two component scores is enough to visualize any possible patterns. The points corresponds to binary hydrides located in the ternary region of the score plot, Fig. 3, are rare earth trihydrides. This is an interesting observation as the rare earth dihydrides show pattern similar to other binary hydrides present in the score plot while rare

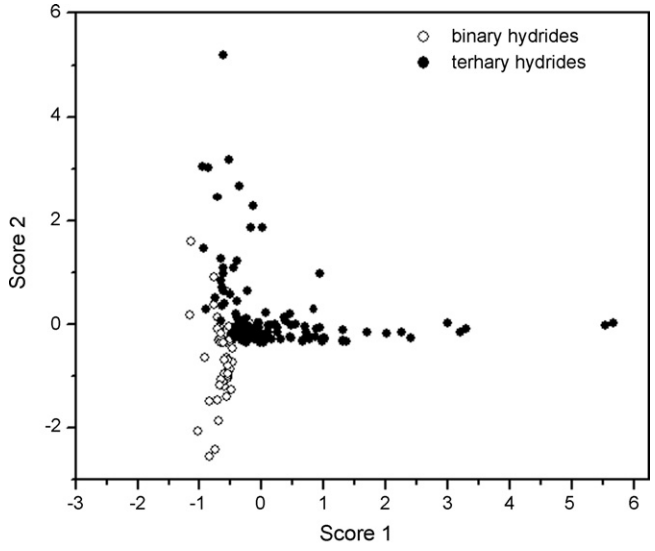

Fig. 3. Plot of score 2 versus score1of a set of data with both binary and ternary hydrides.

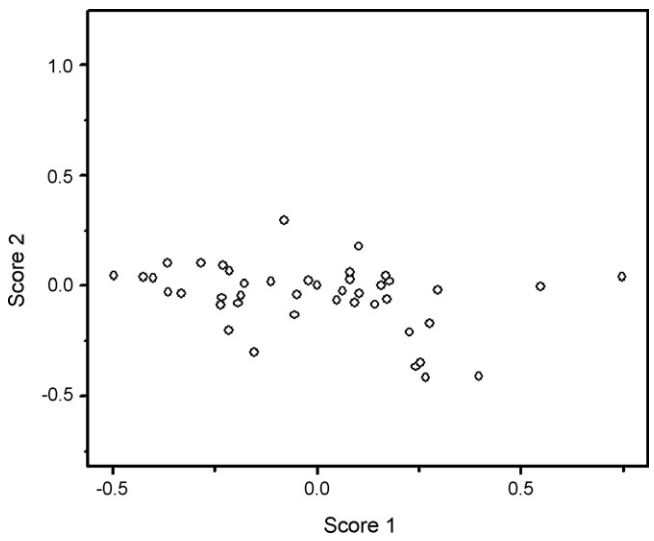

Fig. 4. Plot of scores of first two principal components for binary hydrides.

earth trihydrides show behavior close to ternary hydrides. This is due to the fact that the properties of trihydrides are different from corresponding dihydrides [13]. For example, binary dihydrides are metallic while its trihydrides are semiconducting. It may be concluded from these observations that property of hydrides mostly depends on electronic structure or charge transfer between metal and hydrogen atom than parameters like ionic radii or electro negativity of metal atom. From Fig. 3 it can also be observed that the ternary hydrides exhibits different phenomenon compared to binary hydrides. Therefore we have carried out PCA of binary and ternary hydrides separately. The score plots obtained are presented in Figs. 4 and 5. The outliers found in these plots can be due to erroneous data for corresponding compounds.

4.2. Metal versus metal hydride properties

Estimation of different thermodynamic properties is required to determine the stability of a hydride for suitable technological applications. In general hydride formation is accompanied by a phase transformation of the metal structure which affects their properties. Therefore it is important to consider properties of both metal and metal hydride to understand the how the hydrogen influence

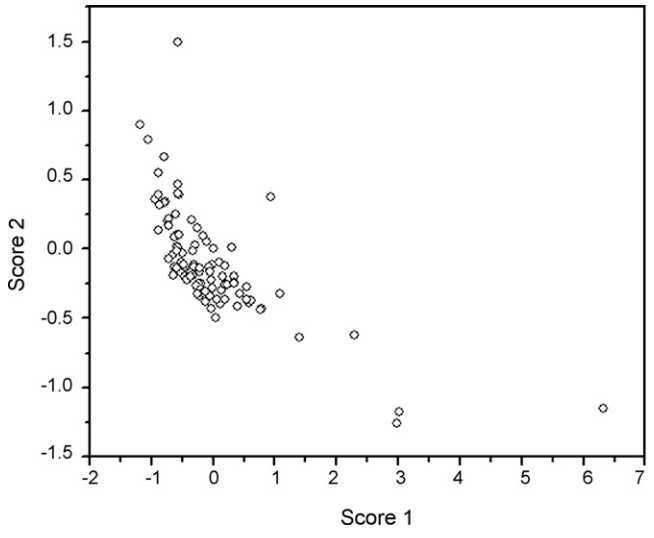

Fig. 5. Plot of scores of first two principal components for ternary hydrides.

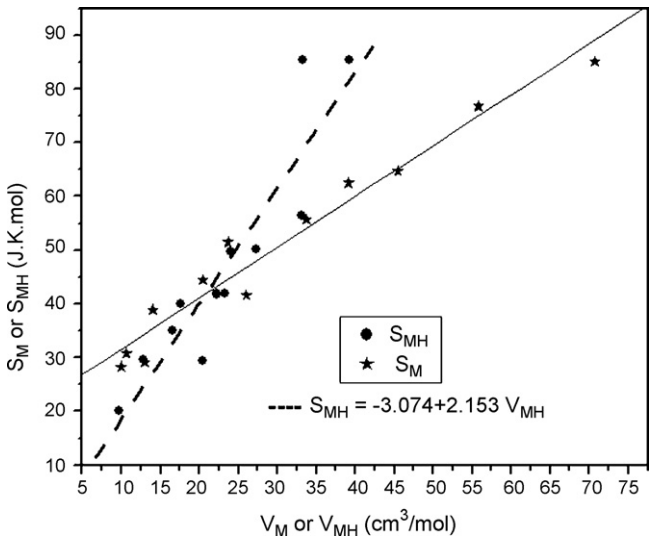

Fig. 6. A comparison of entropy versus molar volume of metals and metal hydrides. Subscript M denotes metal and MH denotes metal hydride.

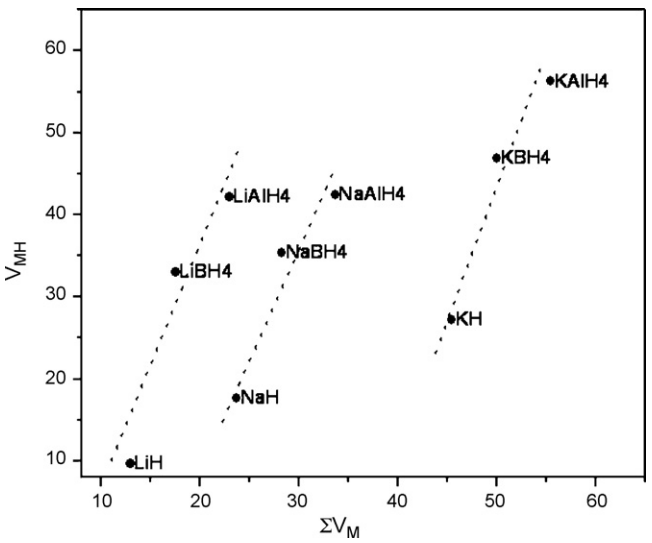

Fig. 8. Plot of molar volume of various alkali metal hydrides versus the sum of molar volume of corresponding host metals.

the material properties. A comparative study of various properties (variables) of hydrides and corresponding metals has been carried out and some of the results are shown in Figs. 6–8. The entropy-molar volume relationship (Fig. 6) of hydrides is found to be different from that of host metals. Analyzing the Fig. 6, entropy of a hydride can be related to its molar volume by the simple formula $S_{MH} = -3.074 + 2.153V_{MH}$. Molar volume of a hydride can be represented as $V_{MH} = V_M + V_H + \Delta$, where V_M is the molar volume of metal/alloy, V_H is the molar volume of hydrogen as a metal ($\sim$1.7 cm^3/mol), Δ is molar volume due to charge transfer between metal and hydrogen atoms. There may be an influence of crystal structure on the value of Δ and hence molar volume of hydride [14]. Larger the difference between electro-negativities of metal and hydrogen greater will be the charge transfer effects and hence the change in molar volume. The density of the alkali metal hydrides is higher than the corresponding metal may be partly because the hydrides have fcc (face centered cubic) metal lattice with a packing density of 0.74 compared to 0.68 for corresponding bcc (body centered cubic) metal lattice. The increase or decrease of entropy, density, volume, etc. on hydriding various materials may be a combined effect of structural transformation and charge transfer on hydriding.

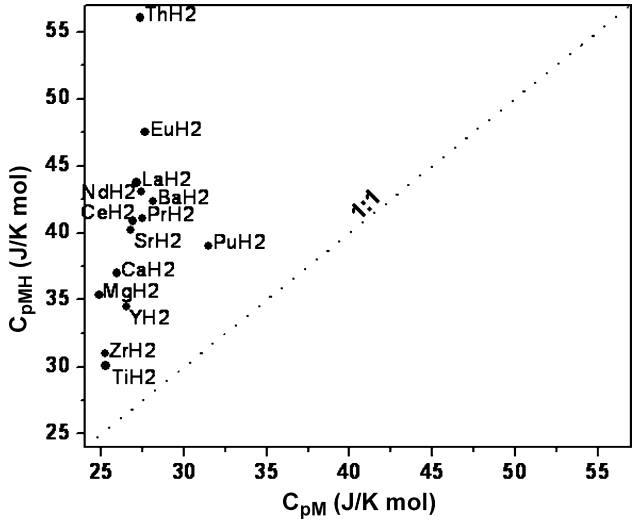

Fig. 7. Plot of specific heat of various binary hydrides versus that of the host metal. The doted line corresponds to the specific heat of metals.

From Fig. 7 it is obvious that hydriding a metal results in large increase of its specific heat which may be due to hydrogen induced optical vibration [15]. The hydrides which contain elements of same group or period also show some similarity in their properties. Plot of molar volume of various alkali metal hydrides versus the sum of molar volume of corresponding host metals is shown in Fig. 8, which suggests that there may be an interrelationship between crystal chemistry and hydrogen induced properties. Hydrides having similar symmetry should show interrelation among their properties which may vary from those of different symmetry.

5. Conclusion

Entropy, molar volume, specific heat and hydrogen content of both binary and ternary metal hydrides were analyzed with PCA. A comparison of properties between metals and their corresponding hydrides gives insight to a combined effect of charge transfer and structural transformation. The specific heat of binary hydrides were higher than that of corresponding metals, whereas the molar volume and entropy of certain hydrides were less than that of corresponding metals which suggests an interrelationship between crystal chemistry and hydrogen induced properties. Entropy of a hydride can be related to its molar volume by the simple formula $S_{MH} = -3.074 + 2.153V_{MH}$.

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References

[1] D. Chandra, J.J. Reilly, R. Chellappa, J. Miner. Met. Mater. Soc. 58 (2006) 26–32.
[2] I. Dincer, Int. J. Hydrogen Energy 27 (2002) 265–285.
[3] S. Wold, K. Esbensen, P. Geladi, Chemom. Intell. Lab. Syst. 2 (1987) 37–52.
[4] R.E. Melvin, P. Patrik, J. Chromatogr. A 994 (2003) 13–36.
[5] K. Heberger, K. Milczewska, A. Voelkel, Colloids Surf. A: Physicochem. Eng. Aspects 260 (2005) 29–37.
[6] W.R. Fawcett, T.M. Krygowski, Can. J. Chem. 54 (1976) 3283–3292.

[7] E.R. Malinowski, Factor Analysis in Chemistry, second ed., Wiley, New York, 1991.
[8] M. Otto, Chemometrics: Statistics and Computer Application in Analytical Chemistry, first ed., Wiley-VCH, Weinheim, 1999.
[9] K. Polat, S. Gunes, Appl. Math. Comput. 186 (2007) 898–906.
[10] J. Bajorath, J. Chem. Inf. Comput. Sci. 41 (2) (2001) 233–245.
[11] B. Hess, Phys. Rev. E 62 (6) (2000) 8438–8448.
[12] M. Viana, X. Querol, A. Alastuey, J.I. Gil, M. Menendez, Chemosphere 65 (2006) 2411–2418.
[13] D.K. Misemer, B.N. Harmon, Phys. Rev. B 26 (1982) 5634–5644.
[14] J.V. Straaten, I.F. Silvera, Phys. Rev. B 36 (1987) 9301–9303.
[15] R.K. Kremer, J.K. Cockcroft, H. Mattausch, A. Simon, G.J. Kearley, J. Phys.: Condens. Matter 6 (1994) 4053–4066.