Estimations of Bonding Nature Using Diamagnetic Susceptibility

Journal:	*ChemComm*
Manuscript ID:	CC-COM-03-2015-002351.R1
Article Type:	Communication
Date Submitted by the Author:	13-Apr-2015
Complete List of Authors:	Tomiyasu, Keisuke; Tohoku University, Department of Physics Sato, Toyoto; Tohoku University, Institute for Materials Research Orimo, Shin-ichi; Tohoku University, Institute of Materials Research; Tohoku University, WPI Advanced Institute for Materials Research

Estimation of Bonding Nature Using Diamagnetic Susceptibility

Keisuke Tomiyasu,[*a] **Toyoto Sato,**[b] **and Shin-ichi Orimo**[b,c]

Received Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
First published on the web Xth XXXXXXXXXX 20XX
DOI: 10.1039/b000000x

A chemical bond includes both covalent and ionic characteristics. We develop an experimental method to estimate the degree of each contribution based on magnetic susceptibility measurements, in which Pascal's scheme for Larmor diamagnetism is combined with the electronegativity. The applicability to metal hydrides is also shown.

A proper comprehension of the nature of covalent and ionic bonds is indispensable toward understanding the properties of materials.[1] All functions with phase transition, reaction, and dissolution processes are accompanied by the modification and breaking of bonds, as are protonic and ionic superconduction. Both covalent and ionic characteristics coexist in a bond, and the degree of covalence can be predicted based on the electronegativity difference between the two bonding elements.[1]

Significant advances have been made thus far to estimate this degree both theoretically and experimentally. Currently, charge distributions and bonding characteristics can be accurately calculated in density-functional theories and orbital overlap and Hamilton population analyses for many systems.[2,3] Combination of X-ray and neutron diffraction can experimentally yield charge distributions even for hydrogens.[4] Photoemission and X-ray spectroscopies provide electronic energy structures,[5] allowing one to analyze the bonding characteristics.

However, particularly for hydrogen materials, not only neutron but also X-ray experiments require the precious beamtime in large facilities because of the weakest X-ray scattering intensity, and available methods are limited for the purpose of many prompt trials and errors necessary for material designs in laboratory. Thus, besides these advanced techniques, if a laboratory-based simple estimation method is developed, this could open up research opportunities to further efficiently use the beamtime and forward the material designs with many trials and errors.

One of the best candidates for the method may be using the Larmor diamagnetic susceptibility (χ_{LD}, LDS), which is closely related to the bonding states and has been successfully described in terms of Pascal's constants in various systems:[6–10]

$$\chi_{\mathrm{LD}} = \sum_i \chi_{\mathrm{core}}(i) + \sum_\nu \lambda_\nu(\nu) \qquad (1)$$

where $\chi_{\mathrm{core}}(i)$ denotes the LDS of the valence core in atom i and $\lambda(\nu)$ is a correction term for the bond ν depending on the bonding state. When using ionic χ_{core} values, λ approaches zero in the case of ionic materials and deviates from zero in the case of covalent materials. Intuitively, this second term means that covalent bonding traps electrons, suppresses their motions, and reduces the diamagnetic induction current. This, in turn, suggests that the degree of this suppression in the LDS could potentially provide an experimentally observable index by which to estimate bonding characteristics. Moreover, magnetic-susceptibility measurements are experimentally simple, applicable to all the three phases of gases, liquids, and solids, insensitive to the subtle nature of the surface, and able to be used to detect signals from the electrons in hydrogen.

In this study, we develop a method to estimate the degree of covalence in a bond using LDS. To check the method, we mainly use literature databases of LDS[10,11] and add our LDS data for some hydrides and referential ionic-bonding fluorides. The experimental details are summarized in the final paragraph.

First, Pascal's scheme was reformulated to avoid the use of Pascal's constants, since their many revisions can, in principle, cause ambiguity. Furthermore, since Eq. (1) consists of two variables, χ_{core} and λ, of which the assignment of the values can be usefully optimized in a series of desired materials,[7] the covalent-bonding effect could be unevenly distributed into the χ_{core} and λ components among unrelated materials.

Therefore, to confine the covalent-bonding effect to a single parameter, we reformulated Eq. (1) as

$$\chi_{\mathrm{LD}} = \sum_i \chi_{\mathrm{ref}}(i) + \Delta\chi_{\mathrm{LD}}, \qquad (2)$$

where $\chi_{\mathrm{ref}}(i)$ denotes the referential theoretical LDS for an ideal ionic form of atom i and $\Delta\chi_{\mathrm{LD}}$ is the deviation from this

---

† Electronic Supplementary Information (ESI) available: Numerical data list. See DOI: 10.1039/b000000x/

[a] *Department of Physics, Tohoku University, Aoba, Sendai 980-8578, Japan. E-mail: tomiyasu@m.tohoku.ac.jp*
[b] *Institute for Materials Research, Tohoku University, Aoba, Sendai 980-8577, Japan.*
[c] *WPI-Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, Aoba, Sendai 980-8577, Japan.*

value corresponding to a covalent-bonding-effect parameter. The meaning of χ_{ref} is basically identical to χ_{core}, but the numerical value of χ_{ref} is fixed as the ideal ionic value for valence core. In this sense, theoretical values will be suitable of χ_{ref}. Here, a set of Pauling's theoretical values is used.[12] Pauling reported that his theoretical values coincide with experimental LDS values for rare gases with no covalent bonding, although they do not hold for other materials,[12] implying that the covalent-bonding effect could be extracted using his values as χ_{ref}.

Then, $\Delta\chi_{\text{LD}}$ is described by

$$\Delta\chi_{\text{LD}} = \alpha \left| \sum_i{}' \chi_{\text{ref}}(i) \right|, \tag{3}$$

where α denotes the aforementioned degree that covalent bonding suppresses the ideally ionic LDS and α is a dimensionless quantity to correlate with the similarly dimensionless electronegativity. Further, $\sum_i'$ denotes a summation over the atoms constituting the bonds, which have the relatively most covalent character in a material. For example, for NaCl, $\chi_{\text{LD}} = \{\chi_{\text{ref}}(\text{Na}^+) + \chi_{\text{ref}}(\text{Cl}^-)\} + \alpha|\chi_{\text{ref}}(\text{Na}^+) + \chi_{\text{ref}}(\text{Cl}^-)|$ and for the complex hydride $NaAlH_4$, in which Na^+ and the predominantly covalent $[AlH_4]^-$ are ionically bonded,[13–15] $\chi_{\text{LD}} = \chi_{\text{ref}}(\text{Na}^+) + \chi_{\text{ref}}([\text{AlH}_4]^-)$, where $\chi_{\text{ref}}([\text{AlH}_4]^-) = \{\chi_{\text{ref}}(\text{Al}^{3+}) + 4\chi_{\text{ref}}(\text{H}^-)\} + \alpha|\chi_{\text{ref}}(\text{Al}^{3+}) + 4\chi_{\text{ref}}(\text{H}^-)|$.

Next, we examined the relationship of α to the electronegativity difference between two bonding elements, $\Delta\chi_{\text{EN}}$, for about 90 inorganic materials using literature χ_{LD} values.[10,11] Figure 1 shows a plot of $\Delta\chi_{\text{EN}}$ versus α. The table of numerical data is summarized in Supplemental Material. Overall, α increases with decreasing $\Delta\chi_{\text{EN}}$, as depicted by the green area into which almost all the symbols fall; amazingly, a certain relationship is recognized commonly for many materials. This demonstrates that the $\Delta\chi_{\text{EN}}$ vs. α plot can function as a relative index of the covalent and ionic bonding nature. We also remark that this finding would simultaneously affords a method for the back-estimation of the LDS from $\Delta\chi_{\text{EN}}$, when no other information, including Pascal's constants, is available for the purpose of diamagnetic corrections, as shown in Fig. 2.

However, the plot is somewhat variable. Following plausible reasons and future improvements may be considered. (1) It would be highly worthwhile to revise and enlarge the set of literature values for χ_{ref}, obtained in the 1920s,[12] using current advanced theoretical methods. (2) Some experimental $\Delta\chi_{\text{LD}}$ values fall outside the green area. Thus, we remeasured the LDS values for LiF, NaF, and AlF_3,[16] which are outside the green area. For comparison, we also re-measured another fluoride KF, which is inside the green area. The lines in Fig. 3(a) show the data for the temperature dependence of the magnetic susceptibility. A negative and almost temperature-independent component, which is the fingerprint of Larmor diamagnetism, and an increasing component in the low temperature range, which is attributable to unavoidable slight magnetic impurities obeying the Curie-Weiss law with almost zero Weiss temperature, are observed. Hence, by subtracting the latter component from the raw data, the LDS component is extracted more clearly, as shown in Fig. 3(b). The revised $\Delta\chi_{\text{EN}}$-α positions obtained from these χ_{LD} are shown as purple solid triangles in Fig. 1. All these fluorides are well within the green area, again supporting the $\Delta\chi_{\text{EN}}$-α relationship and suggesting the effectiveness of the experimental revisions. The reasons for the differences in the LDS values are not presently known, but might be related to sample quality or problems obtaining reliable measurements without SQUID in the past. We believe that, if all the LDS values are revised, the green area will converge more.

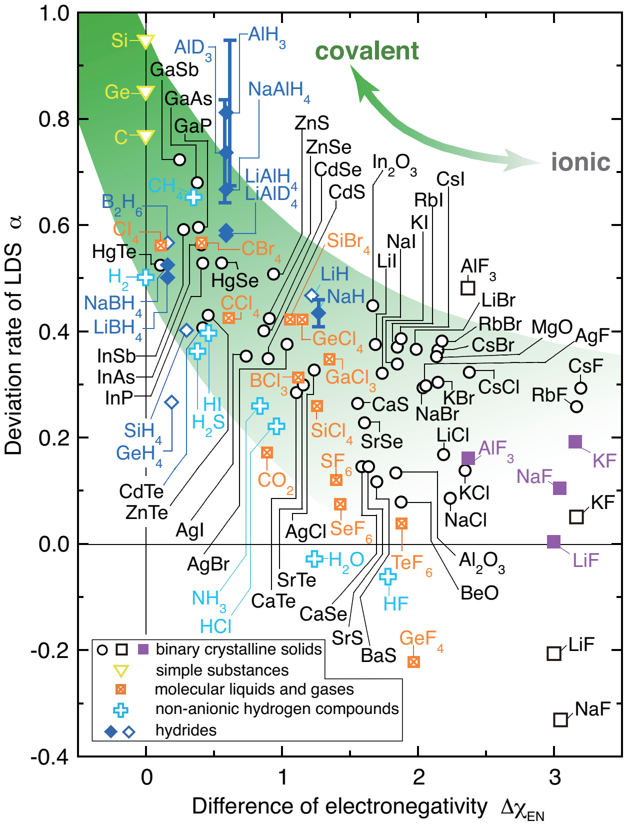

Fig. 1 (Color online) Plot of electronegativity difference $\Delta\chi_{\text{EN}}$ versus LDS deviation rate α. The green area is a guide to the eye. The positions passing through the middle of the green area are phenomenologically described by $\alpha_c = 0.66\exp(-0.53\Delta\chi_{\text{EN}})$. The solid triangle and diamond symbols denote data measured for this paper, in which the errors for three hydrides are shown by vertical bold bars, those for the other materials are within the symbol sizes, and the right (left) error bar in the upper left quadrant is for $AlH(D)_3$. The other symbols denote the literature data.[10,11]

Finally, we apply this LDS method to metal hydrides. Metal hydrides have recently demonstrated intriguing utility, such as hydrogen absorption/desorption capabilities for high-capacity hydrogen storage and high ionic conductivity for solid-state electrolytes. In fact, the metal-hydrogen bonding nature is closely related to the specific function;[17] hence, the degree of covalence has been a key issue in the study of hydrides.[14,15] Here, we consider the hydrogen-storage materials AH, AMH$_4$ (A = Li, Na; M = Al, B), and α-AlH$_3$, as well as the corresponding deuterides.

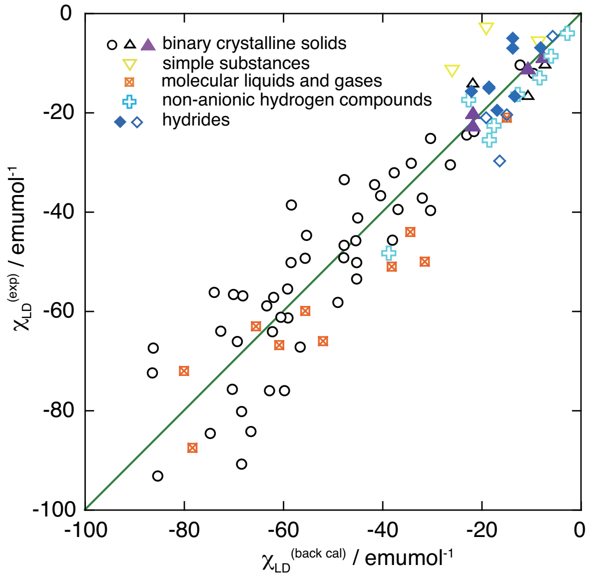

Fig. 2 (Color online) Relationship between back-estimated and experimental χ_{LD}. The former values were calculated using the phenomenological function $\alpha_c = 0.66\exp(-0.53\Delta\chi_{\mathrm{EN}})$ without Pascal's constants.

Figures 3(a) and 3(b) present the data for NaH and AMH$_4$, which were unavailable in the literature. Negative and almost temperature-independent LDS values are again successfully observed. In contrast, Figure 4(a) shows the data for α-AlH(D)$_3$. These susceptibilities are positive, suggesting the slight contamination of the samples by ferromagnetic impurities. To confirm this, we measured the magnetic-field dependence of the magnetization, as shown in Figs. 4(b) and 4(c). As expected, ferromagnetism, which sharply increases with magnetic field and eventually reaches saturation, is observed in addition to the negative-linear (diamagnetic) terms (straight red lines). We also plotted the susceptibilities obtained from the negative-linear terms at several temperatures, as shown in Fig. 4(d). The temperature dependence is weak, confirming that the LDS was extracted for α-AlH(D)$_3$, albeit roughly.

All the $\Delta\chi_{\mathrm{EN}}$-α values obtained for the hydrides are shown in Fig. 1 and are consistent with the other data. This experimentally confirms the following expectations.[14,15] (1) Among the hydrides, LiH and NaH are positioned farthest to the bottom-right side of the plot, demonstrating that they have the most ionic character. (2) LiAlH$_4$ and LiAlD$_4$ are nearly superposed, indicating the similar covalent nature of the Al–H and Al–D bonds, regardless of the isotope.

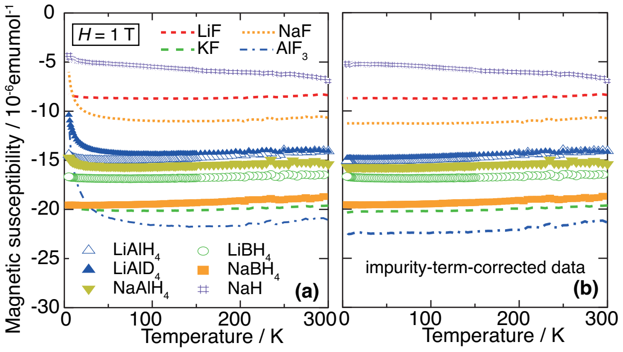

Fig. 3 (Color online) Temperature dependence of measured magnetic susceptibilities for fluorides and hydrides. (a) Raw data. (b) Impurity-Curie-term-subtracted data.

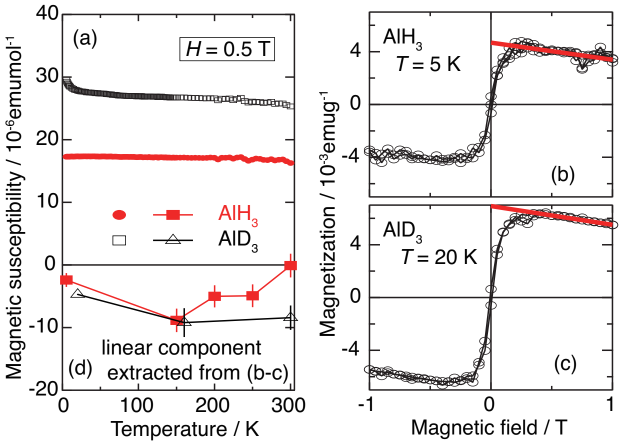

Fig. 4 (Color online) Experimental data for α-AlH$_3$ and α-AlD$_3$. (a) Raw susceptibility data. (b–c) Raw magnetization data. The negatively sloped straight red lines indicate the diamagnetic component. (d) Diamagnetic susceptibility components extracted from the magnetization data.

The bonding nature of Al–H(D) in α-AlH(D)$_3$ has been somewhat debated. In first-principle calculations, the H 1s orbital is almost fully occupied, suggesting its ionic bonding nature,[18,19] whereas the Al 3p valence band is almost the same energy level as the H 1s one, suggesting the covalent bonding nature.[20] Further, soft X-ray Al spectroscopy also suggests a covalent nature.[5] In this regard, Fig. 1 shows that α-AlH(D)$_3$ is positioned toward the top left side of the plot compared to NaH and isomorphic AlF$_3$, beyond the error bars, suggesting that the Al–H(D) bond is much more covalent than the Na–H and Al–F bonds as would be anticipated by electronegativity considerations. Thus, based on all the facts that the H orbital is almost filled with non-negligible covalence[5,18–20] and the Al–H electronegativity difference is as small as the C–Cl one ($\sim$ 0.6), it can be considered that the Al–H(D) bond is classified as a polar covalent bond as in CCl$_4$, neither a normal ionic bond nor a normal covalent bond.

In summary, we have developed a laboratory-based simple experimental method to estimate the degree of covalent and ionic bonding by magnetic susceptibility measurements. A relationship was found between LDS and electronegativity for many inorganic materials including hydrogen materials. An explanation was experimentally obtained with respect to the bonding nature in alane.

Experiments.– Magnetization measurements were performed using direct-current superconducting quantum interference device (SQUID) magnetometers maintained by the Center for Low Temperature Science, Tohoku University. Tested samples included powdered LiF (99.98% purity), NaF (99.99%), AlF$_3$ (99.9%), NaH (95%), LiAlH$_4$ (97%), LiAlD$_4$ (90%), NaAlH$_4$ (93%), LiBH$_4$ (90%), and NaBH$_4$ (98%), purchased from Sigma Aldrich, and powdered KF (99.5%), purchased from Kanto Kagaku. Powdered α-AlH$_3$ and α-AlD$_3$ were synthesized via the chemical reactions of LiAlH$_4$ and LiAlD$_4$ with AlCl$_3$ in diethyl ether, respectively.[21,22] Thin gelatin capsules were filled with the samples ($\sim$100 mm^3) for measurement. Background correction was made by subtracting the signal for an empty capsule from the signal for the sample-filled capsule.

We thank Dr. S. Takagi for the discussion and Dr. K. Iwasa and Mr. M. Onodera for their encouragement. This study was financially supported by Grants-in-Aid for Young Scientists B (22740209, 26800174, and 26820313) and Scientific Research (S) (2522091) from the MEXT of Japan and by the Inter-university Cooperative Research Program of the Institute for Materials Research (IMR) and the Integrated Project of ICC-IMR at Tohoku University.

References

1 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, New York, 3rd edn, 1960.

2 T. Hughbanks and R. Hoffmann, *J. Am. Chem. Soc.*, 1962, **105**, 3528.

3 R. Dronskowski and P. E. Blöchl, *J. Phys. Chem.*, 1993, **97**, 8617.

4 For example, R. Kiyanagi, A. Kojima, H. Kimura, M. Watanabe, Y. Noda, T. Mochida and T. Sugawara, *J. Phys. Soc. Jpn.*, 2005, **74**, 613.

5 Y. Takeda, Y. Saitoh, H. Saitoh, A. Machida, K. Aoki, H. Yamagami, T. Muro, Y. Kato and T. Kinoshita, *Phys. Rev. B*, 2011, **84**, 153102–1–4.

6 J. H. van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Oxford Univ. Press, London and New York, 1932.

7 P. W. Selwood, *Magnetochemistry*, Interscience Publishers, New York, 1943.

8 J. A. Pople, *J. Chem. Phys.*, 1962, **37**, 53.

9 J. A. Pople, *J. Chem. Phys.*, 1962, **37**, 60.

10 D. J. Chadi, R. M. White and A. Harrison, *Phys. Rev. Lett.*, 1975, **35**, 1372.

11 W. M. Haynes, in *CRC Handbook of Chemistry and Physics*, ed. W. M. Haynes, CRC Press, Boca Raton, 95th edn, 2014, ch. 4, pp. 130–135.

12 L. Pauling, *Proc. R. Soc. Lond. A*, 1927, **114**, 181.

13 B. C. Hauback, *Z. Kristallogr.*, 2008, **223**, 636–648.

14 S. Orimo, Y. Nakamori, J. R. Eliseo, A. Züttel and C. M. Jensen, *Chem. Rev.*, 2007, **107**, 4111–4132.

15 A. Unemoto, M. Matsuo and S. Orimo, *Adv. Funct. Mater.*, 2014, **24**, 2267–2279.

16 G. W. Brindley and F. E. Hoare, *Proc. R. Soc. Lond. A*, 1935, **53**, 342.

17 J. N. Huiberts, R.Griessen, J. H. Rector, R. J. Wijngaarden, J. P. Dekker, D. G. de Croot and N. J. Koeman, *Nature*, 1996, **380**, 231.

18 A. Agyuayo and D. J. Singh, *Phys. Rev. B*, 2004, **69**, 155103–1–5.

19 M. J. van Setten, V. A. Popa, G. A. de Wijs and G. Brocks, *Phys. Rev. B*, 2007, **75**, 035204.

20 X. Ke, A. Kuwabara and I. Tanaka, *Phys. Rev. B*, 2005, **71**, 184107.

21 F. M. Brower, N. E. Matzek, P. F. Riegler, H. W. Rinn, C. B. Roberts, D. L. Schmidt, J. A. Snover and K. Terada, *J. Am. Chem. Soc.*, 1976, **98**, 2450–2453.

22 K. Ikeda, S. Muto, K. Tatsumi, M. Menjo, S. Kato, M. Bielmann, A. Züttel, C. Jensen and S. Orimo, *Nanotechnology*, 2009, **20**, 204004–1–4.