Nitrogen dissolution in Liquid Ga and Fe at high pressure by *ab Initio* analysis – application to crystallization of GaN and BN

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Abstract ()

Presently available experimental data indicate that very high solubility of nitrogen in Fe can be achieved in contrast to III group metals (Ga, In, Al) where the solubility is orders of magnitude lower. In this study, dissolution of molecular nitrogen in Ga and Fe metals was investigated by *ab initio* calculations. It was found that both metals strongly attract nitrogen that leads to N_2 molecule decomposition before dissolution. However the N bonding inside these solvents is different. For Ga it is between *Ga4s* and *Ga4p* and *N2p* states whereas for Fe this is by *N2p* states to *Fe4s, Fe4p* and also *Fe3d* states. Accordingly, the calculated energy of dissolution of molecular nitrogen for arbitrary chosen starting atomic configurations, was 0.535 eV/mol. and -0.299 eV/mol. for Ga and Fe, respectively. Expressions for configurations optimized with molecular dynamics contained additional terms, but the difference between the corresponding energy values, 1.107 eV/mol. and 0.003 eV/mol was similar. Full thermodynamic analysis of chemical potential was made employing entropy derived terms in Debye picture. As it has been confirmed, the Debye temperatures are similar: for Ga, $\theta_D = 552\ K$ and for Fe, $\theta_D = 512\ K$. These values indicate that temperature dependent terms are large but not much different, their contribution is: $G_{S-therm} = -0.488\ eV$ and $\Delta G_{S-therm} = -0.475\ eV$ at *T = 1000 K* for Ga and Fe respectively. The entropy dependent terms were obtained ~~by~~ via normal conditions path to avoid singularity of ideal gas entropy at zero K. From these data, nitrogen solubility was obtained, being indeed much higher for Fe than for Ga at similar temperature. In ideal solution approximation, the N concentration in Ga was about $3 \times 10^{-3}\ at\ fr$ at $T = 1800\ K$ and $p = 10^4$ bar whereas for Fe, it was about $9 \times 10^{-2}\ at\ fr$. at the same conditions, which is in very good agreement with experimental evaluations. The high solubility in iron indicates that liquid Fe could be perspective solvent to crystallize GaN from metallic solution at high pressures of nitrogen.