

ORIGIN OF NEGATIVE THERMAL EXPANSION IN CUBIC ZrW_2O_8 , $ZrMo_2O_8$ AND HfW_2O_8 : HIGH PRESSURE INELASTIC NEUTRON SCATTERING STUDY

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The compounds ZrW_2O_8 , $ZrMo_2O_8$ and HfW_2O_8 are of considerable interest due to their large isotropic negative thermal expansion (NTE) over a wide range of temperatures up to 1050 K, 600 K and 1050 K respectively. Thermal expansion in insulating materials is related to the anharmonicity of lattice vibrations. The key parameters, known as Gruneisen parameters, are obtained from the volume dependence of phonon frequencies. We have carried out lattice dynamical calculations for these compounds using a transferable interatomic potential. The phonon frequencies as a function of wave vectors in the entire Brillouin zone and its volume dependence in quasiharmonic approximation are calculated using a program developed by us. The calculations predicted that large softening of the phonon spectrum involving librational and translational modes below 10 meV would be responsible for NTE in these compounds. In order to check our prediction we have carried out high-pressure inelastic neutron scattering experiments at several pressures up to 2.5 Kbar on polycrystalline samples of ZrW_2O_8 and $ZrMo_2O_8$ using IN6 spectrometer at ILL, France. In case of ZrW_2O_8 at 1.7 Kbar, phonon softening of about 0.1-0.2 meV is observed for phonons below 8 meV. Similar shift is observed for cubic $ZrMo_2O_8$ at 2.5 Kbar. The Gruneisen parameters of phonon modes have been determined as a function of their energy. The experiment validates our lattice dynamical calculations.

Keywords: THERMAL EXPANSION, HIGH PRESSURE, PHONON

X-RAY DIFFRACTION EVIDENCE OF SOME LIFSHITZ TRANSITIONS

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Lifshitz electronic transitions manifest as anomalies in various physical properties. However, many of the anomalies due to this subtle transition are difficult to identify or analyze due to the smallness of the anomalies and their sensitivity to temperature. One of the expected anomalies is in the compressibility. However, its identification by the X-ray diffraction technique has been difficult in the past, especially in the absence of structural transformation, essentially due to the lack of precision in the measured P-V data. With the availability of synchrotron sources and diamond anvil cells, and with incorporation of 2-dimensional imaging plate area detector, it is now possible to collect accurate angle dispersive X-ray diffraction (ADXRD) data at close intervals of pressure. We have recently detected the signatures of the Lifshitz transitions in AuX_2 ($X=In, Ga$) compounds by collecting accurate ADXRD data with Elettra synchrotron source. The anomalies which are hardly discernible in the measured P-V curve become prominent when transformed into the universal equation of state. Our interpretations are supported by the detailed electronic band structure calculations of $AuIn_2$, $AuGa_2$, and zinc by state of the art first principles methods. In case of high pressure behaviour of Zn, this method has been crucial in resolving the controversy regarding the high pressure anomalies associated with the Lifshitz transitions.

Keywords: LIFSHITZ TRANSITION, EQUATION OF STATE, HIGH PRESSURE

CRYSTALLIZATION BEHAVIOR OF $CoSb_3$ THIN FILMS

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Cobalt triantimonide $CoSb_3$ crystallizes in the skutterudite type structure (S.G.: $Im-3$). This structure consists of trigonally distorted $[CoSb_6]$ -octahedra building an infinite three-dimensional array. Sb atoms show a rectangular arrangement. Due to large voids within the structure (site 2a), $CoSb_3$ is able to act as host for interstitial atoms. High thermoelectric power and low conductivity values were found for bulk filled skutterudites making them attractive for thermoelectric applications. The structural and thermal behavior of bulk material has also been reported whereas structural investigations on thin films are rare. Films of $CoSb_3$ and the ternary doped system $(Co,Fe)Sb_3$ with Fe atoms on the Co site were deposited 200 nm in thickness onto oxidized Si(100) substrates by dc-magnetron sputtering. These films are amorphous in the as-deposited state. The crystallization behavior of the films was investigated by means of in-situ high-temperature X-ray diffraction. The crystallization of $CoSb_3$ is observed at about 435 K for all films. A metastable supersaturated solid solution of $CoSb_3^{+x}$ is formed. The temperature dependence of the lattice parameters is influenced beside the thermal expansion by the decomposition into $CoSb_3 + Sb$. Above 850 K $CoSb_3$ decomposes to $CoSb$ and Sb. Bulk material $CoSb_3$ decomposes peritectically at 1146 K. Thus, thin films and bulk material show a different thermal behavior. Ex-situ X-ray measurements of thin films, which were annealed at different temperatures in evacuated quartz ampoules, were carried out using grazing incidence. The lattice parameter of doped skutterudite $(Co,Fe)Sb_3$ annealed at 773 K is $a=0.9064(3)$ nm, compared to the corresponding value of $CoSb_3$ ($a=0.9040(2)$ nm).

Keywords: THIN FILMS SKUTTERUDITE HIGH TEMPERATURE X-RAY DIFFRACTION

STRUCTURE AND HIGH-PRESSURE TRANSITION OF $MgXO_3$ ($X=Si, Ge, Ti$) ILMENITE UNDER PRESSURES UP TO 30GPa

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Single crystal structure analyses of $MgSiO_3$, $MgGeO_3$ and $MgTiO_3$ with ilmenite-type structure (R-3, $z=6$) were carried out under high pressures up to 30GPa using a newly devised DAC with diamond crystal backing-plate (5.6 x 6.1 x 1.85mm). The DAC provides great advantages for single-crystal diffraction experiments, such as low X-ray absorption, much high-pressure observation than beryllium plate (previous trial over 50GPa), no powder ring, wide 2θ angle, and transparent window. Synchrotron radiation at SPring-8 having a wavelength of $\lambda=0.40772$ Å and was used for the intensity measurements. $MgSiO_3$ ilmenite is stable at pressures over 20GPa and $MgGeO_3$ is over 5GPa but $MgTiO_3$ is stable at ambient pressure. The bulk modulus of three samples are $K_0=224$ GPa for $MgSiO_3$, 180GPa for $MgGeO_3$ and 158GPa for $MgTiO_3$. Bulk modulus of AO6 and BO6 of $MgSiO_3$ are much larger than those of $MgGeO_3$ and $MgTiO_3$. Site volume ratio, $V(AO6)/V(BO6)$, of $MgSiO_3$ is largest in all three, but the ratio decreases with pressure and is shifted toward unity. Deformations of two octahedral AO6 and BO6 are defined by quadratic elongation, $t = \text{Sum}(l/l_0)/2/6$, and angle variance $s_2 = \text{Sum}(\theta - 90^\circ)/11$. The values of AO6 of all three samples become much smaller than that of BO6 with increasing pressure. Interatomic distance between A2+ and B4+ decreases and the repulsive force between them increases. The triangle shared-plane between both octahedra is reduced and accordingly the load pressure on the plane is raised with pressure. $MgGeO_3$ shows a tendency to an order-disorder transition resulting in corundum structure (R3, $z = 6$) at about 20GPa.

Keywords: $MgXO_3$ ($X=Si, Ge, Ti$) ILMENITE STRUCTURE TRANSITION HIGH PRESSURE