

Japan. Heat capacities of $Mn_xFe_{3-x}O_4$ with the composition $x = 1.0, 1.5,$ and 2.0 were measured from 200 to 740 K. λ -Type heat capacity anomalies due to ferri-paramagnetic transition were observed for all the compositions. The transition temperatures were $577, 471,$ and 385 K for the compositions $x = 1.0, 1.5,$ and $2.0,$ respectively, which are in good agreement with the results of magnetic measurements. The difference in heat capacities between the different samples was small except for the temperature range of the transition. The magnetic contribution of the observed heat capacity was obtained by assuming that the heat capacity can be expressed by the sum of the lattice heat capacity $C_l,$ the dilation contribution $C(d)$ and the magnetic contribution $C(m).$ Entropy changes due to the transition were obtained from $C(m)$ as $55.5, 50.7,$ and 49.2 J K⁻¹ mole⁻¹ for the compositions $x = 1.0, 1.5,$ and $2.0,$ respectively. The entropy changes were also calculated by assuming randomization of unpaired electron spins on each ion, but they were from 6 to 10 J K⁻¹ mole⁻¹ smaller than the observed ones. The difference between the experimental and the calculated values is roughly explained by taking into account the cation-exchange reaction between the tetrahedral and the octahedral sites in the spinel structure.

Observation of a Phase Transition in ThBr₄ and ThCl₄ Single Crystal by Far Infrared and Raman Spectroscopy Study. S. HUBERT*, P. DELAMOYE, S. LEFRANT, M. LEPOSTOLLEC, AND M. HUSSON-NOIS, Laboratoire de Radiochimie, Institut de Physique Nucléaire, B.P. 1, 91406 Orsay, France. At 4 K the visible and infrared absorption and emission spectra of U^{4+} in $ThBr_4$ and $ThCl_4$ single crystals are not very consistent with what is predicted by the selection rules for the room-temperature structure. Thus we investigated Raman scattering in the temperature range 10 – 300 K to look for a structure change and obtain a better understanding of the spectroscopy of U^{4+} in $ThBr_4$ and $ThCl_4.$ At room temperature, the observed Raman lines have been assigned on the basis of a D_{4h} factor group analysis. The study of the temperature dependence of the Raman spectra permitted us to discover phase transitions of $ThBr_4$ and $ThCl_4$ at 95 and 70 K, respectively. The splitting observed for the strongest E_g symmetry mode shows a lowering of the symmetry below the transition point. Powder X-ray diffraction at 77 K of hygroscopic $ThBr_4$ is being carried out to determine the low-temperature structure.

Chemical Diffusion in Intermediate Phases in the Lithium–Tin System. C. JOHN WEN AND ROBERT A. HUGGINS*, Department of Materials Science and Engineering, Stanford University, Stanford, California 94305. The compositional variation of the chemical diffusion coefficient in the six intermediate phases $LiSn, Li_2Sn_3, Li_5Sn_2, Li_{13}Sn_5, Li_7Sn_2,$ and $Li_{22}Sn_5$ of the lithium–tin system at $415^\circ C$ has been measured. Among these intermediate phases, the phase $Li_{13}Sn_5$ has the highest chemical diffusion coefficient, varying with composition from 5.01×10^{-5} to 7.59×10^{-4} cm²/sec at that temperature. Combining this information with coulometric titration curves (EMF versus composition), the self-diffusion coefficient of lithium has also been determined in the various intermetallic phases as a function of composition under the assumption that the tin atoms do not move appreciably compared with the lithium atoms. The lithium self-diffusion coefficient in the phase $LiSn$ is lower than those in the more lithium-rich phases by one order of magnitude. This result is discussed in terms of the difference between the crystal structures of $LiSn$ and the other lithium-rich phases in the lithium–tin system.

Bulk Magnetic and Neutron Diffraction Data for the Pyrochlore Yb₂V₂O₇: Evidence for Ferromagnetic Coupling between Yb³⁺ and V⁴⁺ Moments. LYNNE SODERHOLM, J. E. GREEDAN*, AND M. F. COLLINS, Institute for Materials Research McMaster University, Hamilton, Ontario L8S 4M1, Canada. Bulk magnetic data for the pyrochlore material $Yb_2V_2O_7$ have been redetermined and compared with existing literature values. Susceptibility data from 300 to 77 K can be interpreted in terms of Curie–Weiss behavior above about 170 K, yielding the parameters $C_m = 6.0$ cm³ mole⁻¹ K⁻¹ and $\theta_c = -20$ K. This θ_c is slightly more negative than values reported previously. The saturation moment at 4.2 K is $5.3 \pm 1 \mu_B,$ significantly greater than that reported previously. The magnetization versus temperature curve shows evidence for the ferromagnetic ordering of the V^{4+} sublattice at 73 K and the ferromagnetic ordering of the Yb^{3+} sublattice at about 30 K. The shape of the magnetization–temperature curve is most easily interpreted in terms of ferromagnetic coupling between the V^{4+} and Yb^{3+} sublattices. Neutron diffraction data at 7 and 100 K confirm the ferromagnetic model and yield a value of $1.7 \pm 2 \mu_B$ for the Yb^{3+} moment. This reduced moment (free ion = $4.0 \mu_B$) is consistent with crystal-field parameters found for the isostructural $Yb_2Ti_2O_7$ which has a similar lattice constant.