by about 0.025 Å along tetrahedral directions or by applying existing anharmonic theory for thermal motions. Although all ions are on appropriate sites to contribute to anharmonic effects, only a single anharmonic parameter, representing a weighted difference of two individual parameters, could be evaluated. The anharmonic treatment gives substantially better agreement for critical reflections of the class $h + k + 1 = 4n \pm 1$.

IR-Spektroskopische und Rontgenographische Untersuchungen an Thiospinellmischkristallen. H. D. LUTZ AND H. HAEUSELER. Gesamthochschule Siegen, Lehrstuhl für Anorganische Chemie, 593 Huttental-Weidenau, Paul-Bonatz-Str. 9-11, Germany. The effect of the tetrahedral and octahedral coordinated metal atoms and nonmetal atoms on the vibrational spectra of spinels is studied by investigation of mixed crystals and defect spinels like In_2S_3. The following solid solutions of chromium thiospinels and indium sulfides have been prepared and investigated by X-rays and FIR-spectroscopy: $Hg_xZn_{1-x}Cr_2S_4$(I), $ZnIn_xCr_{2-x}S_4$(II), $CdIn_xCr_{2-x}S_4$(III), $ZnCr_2Se_xS_{4-x}$(IV), α-In_2S_3(V), β-In_2S_3(VI), and $Cr_xIn_{2-x}S_3$(VII). The lattice constants of (I), (III), (IV), and (VII) obey Vegard's rule. (III) has a miscibility gap between $x = 0.3$ and $x = 1.8$. The spectroscopic behaviour of the solid solutions (all the 4 peaks of the spinel spectra split or shift) cannot be interpreted on the basis of internal vibrations of different coordination polyhedra. An explanation of the additional peaks in the spectra of the mixed crystals is given according to order of the atoms or distortion of the spinel structure.

Polymorphism and Stability of Some Sodium Cryolites to High Pressures. CARL W. F. T. PISTORIUS. National Physical Research Laboratory, C.S.I.R., P.O. Box 395, Pretoria, South Africa. Na_3VF_6 and Na_3TiF_6 are monoclinic cryolites at ambient conditions and transform to fcc high-temperature phases at 638.5 and 611°C, respectively. The thermal expansion parameters of Na_3AlF_6 and Na_3TiF_6 were measured to ~ 700°C. The monoclinic–cubic transition lines of Na_3AlF_6, Na_3FeF_6, Na_3VF_6, and Na_3TiF_6 were followed to 40 kbar. They rise with pressure with initial slopes and curvatures that increase with increasing crystal radius of the trivalent ion. The transition entropy appears to be R*ln* 4 in all cases. The fcc high-temperature phases are suggested to be disordered with the fluorine atoms distributed among the 96*j* (or the 96*k*) positions of Fm3m, i.e., fourfold disorder of the XF_6 octahedra. Na_3FeF_6 and Na_3CoF_6 appear to contain the trivalent ions in the high-spin state, while Na_3NiF_6 appears to exhibit an equilibrium between high- and low-spin states. Na_3XF_6 can be expected to be less dense than the assemblage $2NaF + NaXF_4$ for trivalent ions larger than Sc^{3+}, and it is therefore improbable that Na_3LnF_6 can be synthesized at high pressure.

New Nonstoichiometric Molybdate, Tungstate, and Vanadate Catalysts with the Scheelite-Type Structure. A. W. SLEIGHT, K. AYKAN, AND D. B. ROGERS. Central Research Department, E. I. duPont de Nemours and Company, Wilmington, Delaware 19898. Phases of the formula $A_{1-x}\phi_xMO_4$ with the scheelite-type structure are described where ϕ represents a vacancy at the A cation site and M is Mo^{6+}, W^{6+}, and/or V^{5+}. Many different univalent, divalent, and trivalent A cations were used in this study. The phases with no defects, i.e., $x = 0$, were known except for those of the type $A^{1+}_{0.5}A^{3+}_{0.5}MO_4$ where A^{1+} is Ag or Tl and M is Mo^{6+} or W^{6+}. Phases with x greater than zero are generally new and were prepared for catalytic studies. An excellent correlation between catalytic properties and defect concentration has been observed.

X-ray Photoelectron Spectroscopic Studies of Solid Electrolytes. T. DICKINSON, A. F. POVEY, AND P. M. A. SHERWOOD. School of Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne, NE1 7RU, United Kingdom. A study of solid electrolytes by X-ray photoelectron spectroscopy reveals that silver (I) and copper (I) compounds generally show very small shifts in electron binding energies. The complex crystal structure of the β-aluminas, however, gives rise to different cation sites which can be distinguished by this technique. Calculations of self-potential show the importance of this term for determining shifts. The possibility of determining the partial ionic charge from the measured shift is also considered.

Synthése sous Haute Pression d'Oxygène d'une Forme Dense Ordonée $FeVO_4$ et Mise en Evidence d'une Variété Allotropique de Structure $CrVO_4$. J. MULLER AND J. C. JOUBERT. Laboratoire des Rayons X, B. P. No. 166—Centre de Tri, 38042—Grenoble Cedex, France. A new dense form of iron vanadate