coefficient which can be deduced is high, but the carrier number is limited through formation of vacancy pairs tending to give 4 coordination for iron.

Surface Instability and Nonstoichiometry of α*-*Fe_2O_3. J. H. W. DeWit,* A. F. Broersma, and M. Stroband, Inorganic Chemistry Department, University of Utrecht, Croesestraat 77A, 3522 AD Utrecht, The Netherlands. The thermodynamic stability region of α-Fe_2O_3 is investigated by thermogravimetric measurements. By means of electron microscopy, the surface of the grains of sintered compacts is shown to be already reduced well within the α-Fe_2O_3 stability region. Based on this information an electrical conductivity model is presented, in which the inhomogeneous character of the nonstoichiometry of the grains is emphasized.

Mössbauer Studies of Thiospinels.III. The System $FeCr_2S_4$–$FeIn_2S_4$. E. Riedel* and R. Karl, Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, D-1000 Berlin 12, Germany. Polycrystalline samples of spinel compounds $FeCr_{2-x}In_xS_4$ have been obtained in the range $0 \leq x \leq 2$. The nonlinear changes of the cell parameters are explained by the nonlinear behavior of the inversion parameter λ according to the ionic distribution $Fe^{2+}_{1-\lambda}In^{3+}_{\lambda}[Cr^{3+}_{2-x}Fe^{2+}_{\lambda}In^{3+}_{x-\lambda}]S^{2-}_4$. Room-temperature ^{57}Fe-Mössbauer spectra exhibit two sets of absorptions for tetrahedrally and octahedrally coordinated Fe, respectively, each consisting of several overlapping doublets of similar isomer shifts but varying quadrupole splittings. The partial intensity of octahedral site Fe is in agreement with λ. The spectra can be understood by accounting for the influence of variable octahedral-site neighbors on tetrahedral-site iron.

Mössbauer Studies of Thiospinels.IV. The System $FeCr_2S_4$–Fe_3S_4. E. Riedel* and R. Karl, Institute für Anorganische und Analytische Chemie, Technische Universität Berlin, D-1000 Berlin 12, Germany. Spinel compounds of the composition $Fe_{1+x}Cr_{2-x}S_4$ with $0 \leq x \leq 0.5$ have been prepared in polycrystalline form. The ionic distribution $Fe^{2+}[Cr^{3+}_{2-x}Fe^{3+}_x]S^{2-}_4$ is derived from both X-ray and ^{57}Fe-Mössbauer data. Room-temperature Mössbauer spectra show the typical behavior of tetrahedral-site Fe^{2+} surrounded by different octahedral-site neighbors. Octahedral-site Fe^{3+} absorbs as a doublet with $\Delta \approx 0.5$ mm/sec. Samples of overall composition $FeCr_2S_4$ consist mainly of a spinel $Fe^{2+}[Cr^{3+}_{2-y}Fe^{3+}_y]S^{2-}_4$, $y \approx 0.02$.

Crystal Data and Phase Transitions of $KLiWO_4$ *and* $KLiMoO_4$. K. Okada* and J. Ossaka, Department of Inorganic Materials, Tokyo Institute of Technology, O-okayama, Meguro, Tokyo 152, Japan. Crystal data and phase transitions of $KLiWO_4$ and $KLiMoO_4$ were investigated using a high-temperature X-ray powder diffractometer. Phase transitions were observed at 350°C for $KLiWO_4$ and 360°C for $KLiMoO_4$. It was found that the room-temperature phases were isostructural with stuffed derivatives of tridymite and the high-temperature phases were isostructural with stuffed derivatives of cristobalite.

Champ de Force et Caracterisation des Liaisons dans Les Niobates et Tantalates de Structure de Type "Blocs 1 × 2." Y. Repelin,* E. Husson, and H. Brusset, Laboratoire de Chimie et Physico-Chimie Minerales, Institut de Chimie Ecole Centrale des Arts et Manufactures, 92290-Chatenay-Malabry, France. The vibrational study of the three families of the niobates and tantalates of "1 × 2 block"-type structure shows that some vibrational frequencies are characteristic of this structure. The relation between the calculated force constants and the structural characteristics permitted us to distinguish the different types of Nb–O and Ta–O bonds from each other, and to establish a relation between the polarizability of the divalent cation and the mode of linkage of the double octahedra in the layer planes. Finally, the comparison of these results with those obtained for other niobates and tantalates of various structures permitted us to determine the relative stability of all these compounds.

Phenomenological and Structural Study of a Low Temperature Phase Transition in the $PbZrO_3$–$PbTiO_3$ *System.* A. Amin,* R. E. Newnham, L. E. Cross, and D. E. Cox, Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802. The Landau–Ginsburg–Devonshire Phenomenological theory has been applied to the $PbZrO_3$–$PbTiO_3$ crystalline solid solution system to explore the behavior of the rhombohedral:tetragonal morphotropic phase boundary in the region below room temperature. The theory suggests that morphotropy is preserved, i.e., that the phase boundary occurs at nearly the same composition right down to 0 K. The rhombohedral ($R3m$)-rhombohedral ($R3c$) phase transition was investigated for a composition $PbZr_{0.6}Ti_{0.4}O_3$ using neutron diffraction. Structures in both phases were refined by the Rietveld profile fitting technique. The transition behavior in this composition was indicative of a diffuse-type phase transition, with a transition temperature somewhere between 250 and 300 K. The diffuse nature of this transition is perhaps due to short-range ordering of Zr and Ti. However, neutron powder diffraction is not ideal for determining critical behavior; therefore, it is difficult to make a quantitative conclusion in this respect. Values of the spontaneous polarization were obtained from the (Zr/Ti) shifts, and compared to those deduced from phenomenological theory.

Synthesis and Structure of an Infinite Chain Form of ZrI_2 (α). J. D. CORBETT* AND D. H. GUTHRIE, Department of Chemistry, Iowa State University, Ames, Iowa 50011. The synthesis of a second polymorph of ZrI_2 has been achieved by a transport reaction between ZrI_4 and zirconium metal under a 750/850°C gradient in a sealed tantalum tube. The black lath-like crystals produced in the 775°C region occur in space group $P2_1/m$ with $a = 6.821(2)$ Å, $b = 3.741(1)$ Å, $\beta = 95.66(3)°$, $Z = 4$. A total of 669 independent reflections with $2\theta \leq 50°$ and $I > 3\sigma(I)$ were measured at room temperature on a four-circle automated diffractometer with monochromatized MoK_α radiation and were corrected for absorption ($\mu = 190$ cm^{-1}). The structure was solved by direct methods and full-matrix least-squares refinement of all atoms with anisotropic thermal parameters to give final residuals $R = 0.064$ and $R_w = 0.079$. This phase is isoelectronic and isostructural with β-$MoTe_2$, a distorted CdI_2-type structure in which the zirconium atoms are displaced 0.440 Å from the octahedral centers along a to form infinite zig-zag metal chains ($d_{Zr-Zr} = 3.182(3)$ Å) parallel to b. The phase is a diamagnetic semiconductor at room temperature ($E_g \sim 0.1$ eV).

Correlation of Metal–Metal Bonding in Halides and Chalcides of the Early Transition Elements with That in the Metals. J. D. CORBETT,* Department of Chemistry, Iowa State University, Ames, Iowa 50011. Values of the average Pauling metal–metal bond order n per metal valence electron (PBO/e) are reported for about 110 metal-rich compounds of transition groups III–VI (including the lanthanides) which are structurally well characterized. The calculations include bond orders over all metal–metal separations with $n > \sim 0.07$ and assume only the presence of closed-shell anions, the Pauling equation $D_n = D_1 - 0.60 \log n$, and D_1 values likewise calculated from the respective metals. Matrix effects—usually anion–anion repulsions that restrict metal–metal bonding—are shown to yield plausible and predictable reductions in PBO/e values, these effects being greater with high nonmetal:metal ratios, large anion or small metallic radii, in M_6X_{12}-type clusters, and in layered and rock-salt-type structures. On the other hand, 32 metal-rich halides and chalcides are found to be relatively free of matrix effects and to be strongly metal–metal bonded relative to their respective metals by the criterion $0.80 \leq$ PBO/$e < 1.05$, these being principally M_6X_8-type clusters and extended (condensed) metal networks. Three special circumstances are considered: reduced metal–metal bonding in the molybdenum chalcides (but not halides) which arises from strong heteroatom bonding and nonmetal repulsions between clusters; a few errant examples with low concentrations of metallic electrons in which core sizes dictate separations (e.g., Ca_2N, PBO/e = 22.4); and some clusters of Nb, Mo, and Mo containing only oxide and fluoride in which nonmetal π contributions evidently give effective bond orders >1.0.

Phase Diagram and Infrared Spectral Investigation of the $2TeO_2 \cdot V_2O_5$–$Na_2O \cdot V_2O_5 \cdot 2TeO_2$ System. Y. DIMITRIEV,* M. ARNAUDOV, AND V. DIMITROV. Higher Institute of Chemical Technology, Sofia - 1156, Bulgaria. The phase diagram of the $2TeO_2 \cdot V_2O_5$–$Na_2O \cdot V_2O_5 \cdot 2TeO_2$ system is studied by X-ray diffraction, ir spectroscopy, and DTA. A new compound with a compositin of $Na_2O \cdot 3V_2O_5 \cdot 6TeO_2$ is established. The ir spectra of the alkaline trivanadates are interpreted. They are considered as structural analogs of the new phase. As a result of this comparison, the postulate is made that the main structural units in the $Na_2O \cdot 3V_2O_5 \cdot 6TeO_2$ compound are V_2O_8 groups, while tellurium is present both in TeO_3 and TeO_4 groups. Conversely to the crystal phases, in glasses the transition from VO_5 toward VO_4 does not proceed through the formation of new structural units of vanadium, but rather a gradual transition of the structure is observed with a change in the composition from $2TeO \cdot V_2O_5$ to $Na_2O \cdot V_2O_5 \cdot 2TeO_2$.