05.2–1   TEMPERATURE DEPENDENCE OF THE TETRAGONAL DISTORTION IN Cu-III-VI$_2$ CHALCOPYRITE COMPOUNDS. By P.Kistaiah, K.Satyanarayana Murthy and K.V.Krishna Rao, Department of Physics, Osmania University, Hyderabad-7, India.

Chalcopyrite compounds (ch) of the type Cu-III-VI$_2$ are ternary analogues of zincblende (zb) type II-VI binary compounds. They are derived from their binary phases by ordered substitution of other group atoms so as to keep an electron-to-atom ratio of 4. Whereas the tetragonal unit-cell of ch-compounds (space group I42d) is formed by roughly doubling the zb-unit cell along a preferred (c-) direction, the ordering may result in a tetragonal distortion defined by $\Delta = 2 - c/a$; 'c' and 'a' being the lattice parameters (Abraham and Bernstein, J.Chem.Phys.(1973) 59, 5415). Because of the axial symmetry of these crystals the linear thermal expansion coefficients α_a and α_c of the lattice parameters 'a' and 'c' respectively, are anisotropic which give rise to a non-vanishing temperature dependence of the tetragonal distortion. Some theoretical treatments of this distortion have been made by several workers (Abraham and Bernstein, J.Chem.Phys.(1973) 59, 5415; Noolandi, Phys.Rev.(1974) B10, 2490; Weaire and Noolandi, J.Phys.(1975) 36, 27) in terms of the two kinds of bindings of Cu-VI and III-VI, taking into account both the covalent and ionic forces. However, these explanations did not predict the temperature dependence of the tetragonal distortion in these compounds.

Recently, we have measured the anisotropic thermal expansion of a large number of Cu-III-VI$_2$ compounds using powder diffractometry. In all these compounds it was found that the lattice parameter 'a' increases more rapidly with increasing temperature than the parameter 'c' and therefore the tetragonal distortion, 2-c/a, increases with increasing temperature. In previous considerations of the trends in the thermal expansion coefficients of the Cu-III-VI$_2$ compounds it has been always assumed that dΔ/dT increases monotonically with increasing Δ (Weaire and Noolandi, J.Phys. (1975), 27; Neumann, Kristall und Technik (1980) 15, 849; Bhar and Samantha, Phys.Rev. (1982) B26, 2275). However, in the light of our present experimental results, it must be concluded that this supposition is incorrect. In the present work, on the basis of free energy considerations with anharmonic contributions included, a model is developed for the temperature dependence of the tetragonal distortion of the Cu-III-VI$_2$ chalcopyrites, which gives a satisfactory interpretation of all the experimental results reported so far.

05.2–2   THE LOCAL ATOMIC ARRANGEMENT AND THERMAL EXPANSION IN THE ALLOYS OF SYSTEM Mn$_{3-x}$Fe$_x$Al. By A.S. Ilyushin, Physics Dept., Moscow State University, Moscow, U.S.S.R.

The local atomic arrangement was studied in the alloys of the system Nm-Fe-Al using X-ray and Mössbauer effect. The crystal structure of alloys is isomorphic to β-Mn with 20 atoms per unit cell in two positions - 8(c) and 12(d). The analysis of hyperfine structure of Mössbauer spectra was made earlier by the present author. It was found that Fe atoms prefer positions 12(d) and parameters of long-range order were measured for alloys Mn-Fe-Al. Low-temperature X-raying demonstrated the absence of distortions of crystal structure in alloys Mn-Fe-Al even at 5K. The thermal expansion of alloys was measured from 5 to 300K. Anomalies exist on the curves of temperature dependence of the lattice parameters for all alloys at temperatures lower than 80K. These anomalies have magnetic nature and show ferrimagnetic ordering. Correlation between Curie Temperatures and long-range order parameters is established.

05.2–3   HIGH-TEMPERATURE CRYSTAL CHEMISTRY OF CALCITE AND MAGNESITE. By S.A. Markgraf and R.J. Reeder, Dept. of Earth & Space Sciences, State University of New York at Stony Brook, Stony Brook, NY 11794, USA.

X-ray intensity data collected for single crystals of calcite (CaCO$_3$) at 24, 200, 400, 600, 750 and 800°C and of magnesite (MgCO$_3$) at 24, 200, 300, 400 and 500°C yield refinements showing structural changes with temperature. Thermal motions of atoms in the CO$_3$ group are analyzed using a rigid-body model as well as with an anisotropic thermal parameter refinement. Thermal parameters calculated from rigid-body parameters agree well with the refined thermal parameters, suggesting that the rigid-body model is a valid description. Results show markedly different behaviors of the CO$_3$ groups in calcite and magnesite, which may account for the negative thermal expansion along $\underline{a}$ for calcite and positive expansion for magnesite.
    The C-O interatomic distance, corrected for libration, increases more rapidly in calcite (1.289 Å(24°C) to 1.313 Å(800°C)) than in magnesite (1.289 Å(24°C) to 1.291 Å (500°C)). Mean thermal expansion coefficients for the Ca-O interatomic distance ($\bar{\alpha}_{Ca-O}$ = 15.2 x 10^{-6} C^{-1}) in calcite and the Mg-O distance in magnesite ($\bar{\alpha}_{Mg-O}$ = 15.8 x 10^{-6} C^{-1}) are comparable to those found in other CaO$_6$ and MgO$_6$ octahedra.
    The temperature range over which calcite was studied is below the proposed transition temperature for CO$_3$ group disordering ($\sim$985°C). At 800°C the libration parameters for the CO$_3$ group are large, and the l=odd reflections are preferentially unobserved (I< 2σ_I). Although the latter has been suggested as indicating disorder, none is found at this temperature.