

21. STRUCTURAL RESULTS FROM METHODS OTHER THAN DIFFRACTION

21.1-3 SITE SYMMETRY INFORMATION IN ELECTRON ENERGY LOSS NEAR EDGE FINE STRUCTURE* By M.M. Disko, J.C.H. Spence & O.F. Sankey, Arizona State University, Tempe, Arizona, 85287 U.S.A.

Electron energy loss near edge fine structure (ELNES) data show features characteristic of the excited atomic species (J. Taftø and J. Zhu, Ultramic. 9, 349 (1982)). The data of Taftø and Zhu consists of K edges in olivine (Mg-oct, Si-tet), spinel (Al-oct, Mg-tet), and orthoclase (Al-tet). Here "oct" specifies that the atom is at an octahedral site with inversion symmetry, and "tet" refers similarly to tetrahedral sites without inversion symmetry. In each case the ELNES data (0 to 20 eV above threshold) for inversion centers show a single, broad (~10eV wide), almost Gaussian feature, while the ELNES data for tetrahedral sites contains several sharp features.

It has been demonstrated that the K edge ELNES can be interpreted as features related to the density of states (DOS) in the presence of the core hole above the Fermi level, superposed on a smooth background that is essentially atomic (R.D. Leapman, L.A. Grunes, & P.L. Fejes, Phys. Rev. B26, 614 (1982)). The ELNES experiments are conducted under conditions where dipole selection rules apply, and hence a 1s core electron makes transitions to final states with p character. The present work extends the work of Taftø and Zhu to materials having less complex geometries. Electronic structure calculations are performed and compared with the new ELNES data to gain an understanding of the correlation between edge shape and site symmetry.

A preliminary study of Be₂C, which is an antiferromagnetic structure, (C atoms at inversion centers, Be-tet) gives results that follow the trend of Taftø and Zhu. A simple tight binding calculation of the Be₂C DOS shows certain peaks present in the Be p-DOS are absent in the C p-DOS above the Fermi level, explaining the extra features at the Be K edge. Efforts are underway to study Mg₂Si, and improve the Be₂C calculation.

Extension of this work to a number of systems should provide a new structural tool that takes advantage of the high spatial resolution available in STEM, and may prove valuable in the study of disordered materials.

* Supported by NSF grant DMR-8002108

21.1-4 SITE SYMMETRIES IN OLIVINES OBTAINED FROM STRUCTURAL AND SPECTROSCOPIC DATA By H. Rager, FB Geowissenschaften, Universität Marburg, Lahnberge, D-3550 Marburg (FRG) and S. Hosoya, Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai, Japan.

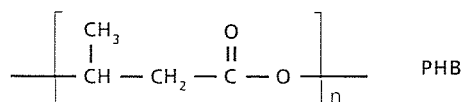
Various attempts have been made to quantify the distortion of the octahedral positions in olivines with varying cations. Usually the distortion is expressed in terms of the cation-oxygen distances and of the angle variance within the octahedra. These terms are obtained from data for refined olivine structures. Measures of the distortion for the M1 and M2 sites have been proposed by several authors. Essentially, they give the same result i.e. the distortion at M1 is approximated by the point symmetry D_{4h} with the main axis along O3-M1-O3 and at M2 by C_{3v} with the main axis along a or b (space group Pbnm).

In the case of paramagnetic cations, present at M1 and M2 in low concentration, the local symmetry can also be obtained by measuring the electron paramagnetic resonance spectra in single crystals. The results obtained in that way are: The local symmetries of Fe³⁺, Cr³⁺ and Ni²⁺ at M1 are D_{4h} (main axis along O2-M1-O2), D_{2h} (no correspondence of the main axis with any cation-oxygen direction), and C_{3i} (main axis along a), respectively. The local symmetry of both Mn²⁺ and Fe³⁺ at M2 is C_{2v} (main axis nearly along M2-O2) and of Cr³⁺ at M2 is D₂ (main axis nearly along a). Thus, the local symmetries at M1 and M2 derived from structural and spectroscopic data differ significantly either in the direction of the main axis or in the local symmetry. This will be discussed.

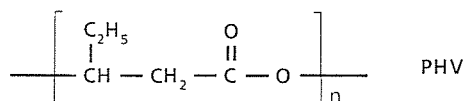
21.1-5 Analysis of Poly(β-hydroxybutyrate-co-β-hydroxyvalerate) Using X-ray Diffraction, NMR Spectroscopy and Differential Scanning Calorimetry

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Poly-β-hydroxybutyrate (PHB) is an important storage material in a variety of bacteria. This optically active polymer is found as crystalline granules (1) in the native bacteria. When isolated from the bacteria and cast into films PHB has mechanical properties similar to those of polypropylene.



Poly-β-hydroxyvalerate (PHV) is also a bacterial storage material but less ubiquitous than PHB.



The crystal structures of these optically active polymers have been previously determined (2,3,4). PHB crystallizes in an orthorhombic unit cell with a = 5.76 Å, b = 13.20 Å and c (fiber axis) = 5.96 Å which contains two antiparallel chains. PHV also crystallizes in an orthorhombic unit cell with a = 9.32 Å, b = 10.02 Å and c (fiber axis) = 5.56 Å again containing two antiparallel chains.

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Recently, we have obtained materials (5) reported to be copolymers with varying comonomer ratios of hydroxybutyrate (HB) to hydroxyvalerate (HV). The ratios of HB to HV run from 98:2 to 53:47 as determined by ^1H NMR. The techniques of x-ray diffraction, NMR spectroscopy (^1H and ^{13}C) and differential scanning calorimetry (DSC) have been used to determine whether these materials are completely random or block copolymers. X-ray diffraction has revealed some interesting peculiarities of the polymer morphology. It appears that for ratios of HB:HV of 4:1 and greater the HV units have little effect on the PHB crystal structure other than to increase the disorder of the crystallites as shown by x-ray diffraction measurements of crystallinity and perfection. At an HB:HV ratio of approximately 1:1 the crystalline structure is the same as that of pure PHV with no indication of any PHB crystallites being present. These results are somewhat unusual in view of the indications from high resolution solution NMR spectroscopy that the copolymers are fully random. It may be that isomorphous replacement of one comonomer by the other occurs in these materials.

References

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5. Materials kindly provided by Dr. Paul Holmes, Agricultural Division, Imperial Chemical Industries, Billingham, U.K.

21.1-6 ELECTRON PARAMAGNETIC RESONANCE OF Ni^{2+} IN FORSTERITE Mg_2SiO_4 . By S. Hosoya, H. Rager and S. S. Hafner, Institute of Mineralogy, University of Marburg, 3550 Marburg, West Germany.

In olivines $(\text{Fe},\text{Mg})\text{SiO}_4$, Ni^{2+} ions may be substituted for Mg and Fe^{2+} at the octahedral sites M1 and M2. According to Rajamani et al. (*Amer. Mineral.* (1975) 60, 292), Bish (*Amer. Mineral.* (1981) 66, 770), and Nord et al. (*Amer. Mineral.* (1982) 67, 1206), Ni^{2+} in synthetic and natural phases with compositions of $1.5 > \text{Ni} > 0.5$, $1.0 > \text{Mg} > 0.3$, and $0.3 > \text{Fe} > 0$ shows strong preference for M1. This is further supported by Annersten et al. (*Amer. Mineral.* (1982) 67, 1212) for synthetic phases $1.8 > \text{Fe} > 0.5$ and $1.5 > \text{Ni} > 0.2$. According to Smyth and Tafto (*Geophys. Res. Lett.* (1982) 9, 1113), exchange kinetics of Ni between M1 and M2 is rapid, exchange being observable in a natural single crystal $\text{Mg}_{1.96}\text{Fe}_{0.18}\text{Ni}_{0.04}\text{SiO}_4$ at temperatures as low as 300°C after heating for 6 days.

We have studied electron paramagnetic resonance of Ni^{2+} at 9.52 and 35 GHz frequencies in a crystal $\text{Mg}_{1.96}\text{Ni}_{0.04}\text{SiO}_4$ grown with the floating zone technique. A strong Ni^{2+} spectrum was observed at 35 GHz which has to be assigned to a position 4a of Pnma because of symmetry reasons. It is, therefore, attributed to M1. The diagonalized terms of the tensor g are $g_x = 2.194$, $g_y = 2.160$, and $g_z = 2.188$. The axial and rhombic fine structure terms are $D = -1186.2$ GHz and $E = -17.37$ GHz, respectively. The value $3D/E = 0.044$ is very small, being indicative of rhombic distortion of M1 in Mg_2SiO_4 by Ni^{2+} .

A Ni^{2+} spectrum at M2 could not be observed. However, because of the distinct geometrical distortion of M2 compared to M1, a higher frequency than 35 GHz may be needed to observe it. We do, therefore, not conclude that Ni^{2+} at M2 is completely absent.

The same crystal was heated at 300°C for 7.5 days, 600°C for 5.5 days, 900°C for 2.5 days, and 1150°C for 1 day. The crystal was quenched after heating. Although precise, relative intensities could not be measured because of lack of the M2 pattern, it was thought that significant Mg, Ni exchange between M1 and M2 would influence the line intensities of the observed M1 spectrum. Neither occurrence of new Ni^{2+} resonance lines nor a change in the intensities of the M1 spectrum could be detected.

21.1-7 VIBRATIONAL SPECTRA AND STRUCTURAL PROPERTIES OF LiNaCO_3 . By Ernst-Jürgen Zehnder

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Isotopic substitution and temperature dependent IR-, FIR- and Ramanspectra are used to get structural information and to discuss anion disorder and structural phase transition in LiNaCO_3 .

An intermolecular vibrational coupling of the carbonate out-of-plane vibration ν_2 is observed in lithium sodium carbonate comparable to those found in carbonates, nitrates and borates with the aragonite structure and in silver carbonate. (E.-J. Zehnder, W. Sterzel, *Spectrosc. Lett.* (1982) 15, 463; E.-J. Zehnder, *J. Mol. Struct.* (1983) 98, 49).

In partially ^{13}C substituted lithium sodium carbonate this coupling results in a fine structure of the infrared active ν_2 band. Our cyclic chain model permits a quantitative description of this fine structure assuming two types of different carbonate ions planar superimposed to form linear chains. The different absorptions can be correlated to single ions, doublets, triplets etc. of one isotopic species in the matrix of the other isotopic ion. The coupling strengths comparable to those in barium carbonate require in chain carbonate-carbonate distances some more than 320pm.