

## 21. STRUCTURAL RESULTS FROM METHODS OTHER THAN DIFFRACTION

21.1-10 X-RAY FLUORESCENCE APPLIED TO MINERALS. RELATIONSHIPS BETWEEN ATOMIC NUMBER OF AN ELEMENT AND ITS ACTUAL PERCENTAGE. By H.S. Villarroel, Centro de Tecnologia - UFPE, Recife, Brazil.

Very often in quantitative analysis of minerals and rocks, only a partial chemical analysis is available. The possibility of estimating some chemical elements by measuring the intensity of X-ray fluorescence as a function of the atomic number has been studied. For this purpose, the concept of normalized intensity is introduced. The percentage of one chemical element can then be found, provided that the percentages of at least two others are known.

Such an approach does not require the use of external reference standards. It is applicable in the analysis of a set of samples with similar matrix. The method has been tested against international standards and applied to several rocks from North-east Brazil.

21.1-11 THE STRUCTURE OF PARAMAGNETIC CENTRES IN NATURAL GLASSES. R.M. Mineeva, L.V. Bershov, A.S. Marfunin, V.V. Nasedkin. Institute of the Geology of Ore Deposits (IGEM), Academy of Sciences of the USSR, Staromonetny 35, 109017, Moscow, USSR.

Different types of natural glasses have been investigated by EPR at 9.5 and 35 GHz frequencies. Narrow lines related to  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  ions were observed as well as broad lines due to magnetic phases.

Deformation of polyhedra with paramagnetic ions has been estimated using superposition model for different kinds of ion position in glass matrix. It was shown that strong crystal field is necessary for the EPR signal with  $g \approx 4.3$  and this crystal field can be created only in the cases when  $\text{Fe}^{3+}$  containing tetrahedra occur at surfaces between clusters corresponding to quartz and cristobalite structure fragments and glass matrix.

It was demonstrated that existence of crystalline nonmagnetic clusters in glasses is possible only with their stabilization by impurity ions. Coordination polyhedra with paramagnetic impurity ions have to be a little larger than sizes of a cavity which is a natural extension of a crystal structure. In such a case the impurity ion blocks up the crystal structure cluster in nonperiodic glass matrix.

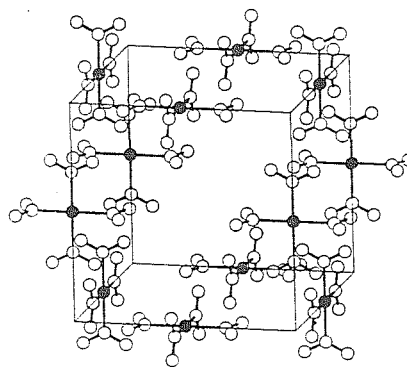
21.1-12 STRUCTURE AND BONDING IN  $\text{Cu}^{2+}$ -NITROCOMPLEXES -X-RAY AND EPR-SPECTROSCOPIC RESULTS. By A. Ozarowski,\* W. Abriel and D. Reinen, Sonderforschungsbereich 127 and FB Chemie der Universität, 355 Marburg, Germany F.R.

A series of new cubic  $\text{Cu}^{2+}$  nitrocomplexes  $\text{M}_3\text{M}'[\text{Cu}(\text{NO}_2)_4]_2 \cdot x\text{H}_2\text{O}$  ( $\text{M}=\text{Rb}, \text{Cs}; \text{M}'=\text{Na}, \text{K}, \text{Rb}$ ) has been prepared. A single crystal X-ray investigation of the compound with  $\text{M}=\text{Cs}$  and  $\text{M}'=\text{K}$  yielded a novel structure with square planar  $\text{Cu}(\text{NO}_2)_4^{2-}$  anions (Fig.1). The cationic part of the structure could not be solved completely because of positional disorder of  $\text{K}^+$  and water. The EPR spectra exhibit a temperature independent isotropic signal at  $g=2.120(3)$  as the result of exchange-coupling between the three sublattices with differently oriented  $\text{CuN}_4$  squares.

Figure 1

The  $\text{Cu}(\text{NO}_2)_4^{2-}$  entities in  $\text{Cs}_3\text{K}[\text{Cu}(\text{NO}_2)_4]_2$ :

$a = 10.950(7) \text{ \AA}$   
Space group  $\text{Fm}\bar{3}$   
Final  $R_w = 0.07$   
Cu-N spacings:  
 $2.01(2) \text{ \AA}$



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EPR single crystal studies of perovskite-type complexes  $\text{M}_2\text{Cd}_{2-x}\text{Cu}_x(\text{NO}_2)_6$  ( $\text{M}=\text{K}, \text{Tl}, \text{Rb}, \text{Cs}$ ) at 9, 35 and 63 GHz and between 298 and 4.2 K revealed strongly anisotropic  $g$ -values as the consequence of a static Jahn-Teller effect and a well resolved Cu- and nitrogen hyperfine structure (Fig.2). In case of the Tl-compound an additional hyperfine-structure due to Tl was observed. At higher  $\text{Cu}^{2+}$ -concentration exchange-coupled signals due to  $\text{Cu}^{2+}$ - $\text{Cu}^{2+}$  pairs are detected. The anisotropic  $g$ ,  $A_{\text{Cu}}$  and  $A_{\text{N}}$  tensors, the observed ligand field transitions as well as further details of the EPR spectra are discussed in terms of Cu-N bonding parameters in a MO-description.

Figure 2

