

SHORT COMMUNICATIONS

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Electron density distribution in MgS. By YOSHIO TAKÉUCHI,* *Department of Earth Sciences, Nihon University, 3-25-40 Sakurajosui, Setagayaku, Tokyo 156, Japan*, SATOSHI SASAKI,† *Photon Factory, National Laboratory for High Energy Physics, Tsukuba, Ibaraki 305, Japan*, KLAUS A. BENTE, *Mineralogisch-Kristallographisches Institut, Universität Göttingen, 3400 Göttingen, Germany*, and KATSUHIRO TSUKIMURA, *Geological Survey of Japan, Higashi 1, Tsukuba, Ibaraki 305, Japan*

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Abstract

MgS, $M_r = 56.37$, cubic, $Fm\bar{3}m$, $a = 5.20182(9) \text{ \AA}$, $V = 140.76 \text{ \AA}^3$, $Z = 4$, $D_x = 2.659 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $\mu = 19.15 \text{ cm}^{-1}$, $F(000) = 112$, $T = 303 \text{ K}$, final isotropic $R = 0.0206$, $wR = 0.0211$ for 109 unique reflections with $F > 3\sigma(F)$. The effective distribution radius (EDR) of the Mg atom was found to be $1.28(2) \text{ \AA}$, yielding a net charge of $+1.50(1)$.

Introduction

In a paper published elsewhere (Sasaki, Fujino, Takéuchi & Sadanaga, 1980), a procedure was introduced to determine atomic net charges from direct integration of the electron density within the sphere of a newly defined radius, around each cation. The radius, which we denoted as the *effective distribution radius* (EDR) (Fujino, Sasaki, Takéuchi & Sadanaga, 1981), can be defined in terms of the radial electron density distribution of the cation. Application of this procedure has so far been confined to oxygen-based compounds (Sasaki, Fujino & Takéuchi, 1979; Sasaki *et al.*, 1980; Fujino *et al.*, 1981; Sasaki, Takéuchi, Fujino & Akimoto, 1982; Haga & Takéuchi, 1982). Here we report the case of magnesium sulfide, MgS, primarily to compare it with the case of isotypic MgO (Sasaki *et al.*, 1979). The cell constant of MgS has been reported as $5.201(5) \text{ \AA}$ (Flahaut, Domange & Patrie, 1962), $5.2036(3) \text{ \AA}$ at 294 K (Güntert & Faessler, 1956), and $5.1913(1) \text{ \AA}$ (Primak, Kaufman & Ward, 1947).

Experimental

The single crystals used for the present study were obtained by the method of chemical vapor transport, using iodine gas (5 mg ml^{-1} free volume) and a silica tube of 15 mm diameter and 150 mm in length; transport gradient 1168–1078 K, crystallization time 5–8 days for *ca* 500 mg MgS. The starting material, MgS, was synthesized at approximately 873 K in an evacuated silica tube, using the elements Mg and S, both of which had a purity of greater than 99.99%. One of the crystals, colourless and transpar-

ent, was ground to the shape of a sphere with radius $85 \mu\text{m}$ and used for the X-ray study.

The measuring device and parameters for X-ray diffraction were: Rigaku AFC-5 four-circle diffractometer, graphite monochromator, Mo $K\alpha$ radiation, 45 kV and 30 mA, cell constant by least-squares fit of eight reflections with $145 < 2\theta < 155^\circ$, ω - 2θ scan technique, range $2\theta < 160^\circ$ ($\sin\theta/\lambda < 1.3857 \text{ \AA}^{-1}$), $h = 14/14$, $k = 14/14$, $l = 0/14$, intensity check by the reflections 200 and 220 measured every 50 reflections, intensity variation $< 2.2\%$ throughout data collection; 1370 reflections measured, Lorentz-polarization, spherical absorption (transmission factors: max. 0.792, min. 0.785) and secondary-extinction corrections (Becker & Coppens, 1974) [$g_{\text{iso}} = 0.015(4) \times 10^{-4}$]; after averaging 1370 reflections ($R_{\text{int}} = 0.033$), 109 unique reflections with $F > 3\sigma(F)$ used for analysis. Atomic scattering factors for Mg^{2+} and S^{2-} were used. Since the values for the latter were not available, they were obtained by extrapolation of those for neutral S and S^- . These two sets of values, together with those for Mg^{2+} and anomalous-scattering parameters were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Isotropic least-squares refinement, using F_o , unit weights, with *RADY* (Sasaki, 1987) converged to a value of $R = 0.0206$; ‡ max. $\Delta/\sigma = 0.000027$, max., min. heights in final $\Delta\rho$ map 0.4, -0.4 e \AA^{-3} , $S = 4.2$. Temperature factors obtained for Mg at the origin and S at $0.0, \frac{1}{2}$, each having point symmetry $m\bar{3}m$, are 0.793(13) and 0.589(8) \AA^2 , respectively. Fourier syntheses were carried out with the program *FRAXY* (Sasaki, 1987), on a Facom M360 MP computer at the Computer Centre of the Photon Factory.

Results and discussion

The radical electron distribution, $U(R)$, of the Mg atom of MgS was obtained by differentiating $C(R)$, the number of electrons in a sphere of radius R , with respect to R (Sasaki *et al.*, 1980). The result is compared to that of MgO (Sasaki *et al.*, 1979) in Fig. 1. The $U(R)$ value in the

‡ Lists of structure factors and numerical values of $U(R)$'s and $C(R)$'s (electron numbers) for both Mg and S have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55879 (4 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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present case has a salient feature in that it exhibits a small but significant hump at around $R = 1.3 \text{ \AA}$ while that of the MgO case falls into the category of *minimum type* (Sasaki *et al.*, 1980). To determine the EDR, we calculated $dU(R)/dR$ for the region $R = 1.0\text{--}1.6 \text{ \AA}$ and applied the procedure we used to determine the EDR for the cases of $U(R)$ for the *flat type* (Sasaki *et al.*, 1980). We thus found $\text{EDR} = 1.28(1) \text{ \AA}$, the error being estimated in terms of the e.s.d.

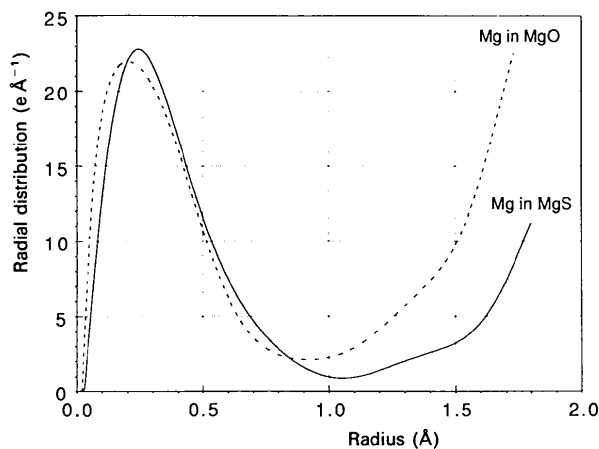


Fig. 1. The $U(R)$ curve for Mg in MgS (solid line) as compared to that in MgO (broken line).

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Molecular dynamics study of the TiO_2 (rutile) and $\text{TiO}_2\text{--ZrO}_2$ systems. By K. FUKUDA, I. FUJII and R. КИТОH, *Inorganic Materials Research Laboratory, UBE Industries Ltd, 1978-5 Kogushi, Ube-city, Yamaguchi 755, Japan*, and I. AWAI, *Department of Electrical and Electronic Engineering, Yamaguchi University, Tokiwadai, Ube-city, Yamaguchi 755, Japan*

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Abstract

The molecular dynamics (MD) method is applied to the simulation of the structural and physical properties of the TiO_2 (rutile) and $\text{TiO}_2\text{--ZrO}_2$ systems. The interatomic potential model consists of Coulomb and repulsive terms between atoms, and an additional Morse potential term for both titanium–oxygen and oxygen–oxygen interactions. The MD simulations have succeeded in reproducing the structural and physical properties of TiO_2 , including the crystal structure and the thermal expansivities. The MD method was further proved successful by its ability to reproduce the observed crystal structure of the $\text{TiO}_2\text{--ZrO}_2$ system.

Introduction

In order to investigate the properties of materials, numerical computation is becoming an increasingly important technique. Computer simulations can be applied to a large variety of materials such as fused salts, glasses

and proteins. However there are not many studies on inorganic materials owing to the difficulty of construction of practical interatomic potential models. Such constructions are one of the most essential parts of molecular dynamics (MD) methods.

For inorganic materials, Matsui (1988, 1990) has reported that the MD method successfully reproduced the available structural and physical properties of the perovskite MgSiO_3 , and he has also investigated the structure of three types of TiO_2 (rutile, anatase, brookite) with the object of predicting the high-temperature and high-pressure behavior, where the crystal structures were successfully reproduced, but the thermal expansivities were smaller than the observed values. The potential function in Matsui's work was composed of Coulomb, van der Waals and a Gilbert (1968) type repulsion term.

TiO_2 (rutile) has a high dielectric constant and a low dielectric loss which are valuable properties for microwave dielectric ceramics (Egerton & Thomson, 1971). The physical properties such as dielectric constant and thermal

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