EFFECT OF SHOCK COMPRESSION ON THE STRUCTURE OF MERCURY OXIDE

I. A. Ovsyannikova, É. M. Moroz, and A. I. Platkov

UDC 541.451:546.49:531.66

The effect of shock compression on the crystal structure and the electron levels in mercury oxide has been studied. On the basis of x-ray spectrometric, x-ray radiographic, and neutronographic examinations, a new sphalerite-type crystal form of mercury oxide with a lattice parameter $a = 5.43$ Å is hypothetically assumed to have appeared as a result.

In the study of materials subjected to shock compression one finds particularly interesting the appearance of modified crystal forms, which are sometimes retained in the metastable state and after the pressure has been relieved. In most cases these modifications are already known ones, which are produced either under high static pressures or under high temperatures. Entirely new modifications appear rarely and, therefore, their study is particularly interesting. An example of such a modification is the brown form of mercury oxide produced for the first time under shock compression [1]. Results of these studies and some properties of this crystal form were reported in [2]. The x-ray L_{III} absorption spectrum of mercury in HgO was examined in [3], where a large energy shift of the absorption limit after shock compression was also detected. Inasmuch as such a shift could not be explained by plastic deformations or defects [2], further studies were undertaken.

It has been shown in [4] that the shift of the x-ray absorption limit is related to a change in the effective coordination charge, along with a change in valence, in the ionization level of the chemical bond, and in the coordination number of the given atom. It has been shown in [2] that the chemical constitution and the valence of mercury do not change as a result of shock compression. Following this conclusion, the shift of the L_{III} absorption limit for mercury in HgO after shock compression is hypothetically attributed in [3] to a local reconfiguration of the oxygen enclosure around mercury toward a higher coordination number.

The authors have made further studies of the brown HgO and have examined the L_{III} absorption spectrum of mercury in HgS, the latter existing in two forms: one hexagonal and analogous to the known HgO form (with a chain structure and a coordination number 2 for mercury referred to sulfur) and in the other form the enclosure around a mercury atom is tetrahedral.

The L_{III} absorption spectra were obtained with a model DRS-2 spectrograph by means of a second-order reflection from the $11\bar{2}0$ system of quartz planes. The position of point L, the center of the absorption band, is shown in Table 1 and is taken here to imply the position of the limit. It can be seen here that an increase in the coordination number for mercury in HgO does, indeed, cause a shift of the L_{III} absorption limit toward longer waves. A calculation of the effective coordination charge for mercury in HgO as well as in HgS and a comparison with measured shifts has shown that, for mercury, such a shift of the L_{III} absorption spectra is a linear function of the effective coordination charge η (Fig. 1), just as in the case of various compounds of other elements [4].

The absorption spectrum of mercury in HgO subjected to shock compression is made up of superposed absorption spectra, namely, those of mercury atoms whose enclosure has not changed and those of mercury atoms whose enclosure has changed. For this reason, the shift of the L_{III} absorption limit toward

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 22, No. 4, pp. 735-738, April, 1972. Original article submitted February 4, 1971.

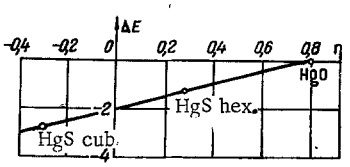

Fig. 1

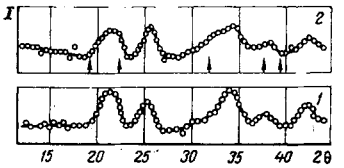

Fig. 2

Fig. 1. Energy shift ΔE (eV) as a function of the coordination charge η.

Fig. 2. Neutronograms of HgO: 1) original; 2) after shock compression. Wulf–Bragg angle θ; intensity I (in relative units).

TABLE 1. Energy at the L_{III} Absorption Limit for Mercury in Its Compounds

Substance	Position of the limit, eV	ΔE, eV	η
HgO original	12298,3	0	0,78
HgS explosive	1295,2	—3,1	
HgS cubic	1295,4	—2,9	—0,30
HgS hexagonal	1297,2	—1,3	0,28
Error	±0,5		

longer waves can be explained by a decrease in the coordination charge of at least some mercury atoms. According to [2], the valency of mercury has not changed; a higher covalence in this case is improbable, since a chain coordination corresponds to the maximum proximity between mercury and oxygen atoms down to a distance approximately equal to the sum of the covalent radii during sp-hybridization (2.03 Å [5]) and further changes in this direction are impossible. Thus, by analogy to the shift of the absorption spectrum of mercury in HgS during changes in the coordination, an extrapolation of the already established $\Delta E = f(\eta)$ relation will lead us to the conclusion that at least one consequence of shock compression could be the appearance of an HgO crystal form with a higher coordination number for oxygen.

A higher coordination number is usually associated with a higher ionization of bonds and with larger interatomic distances. A higher ionization of bonds is, indeed, in evidence in shock compressed HgO, according to the data shown in [2]: an increase in the effective coordination charge from 0.62 to 0.89, as calculated by the Szigetti method, a widening of the forbidden zone from 2.27 to 2.62 eV, an increase in the refractive index from 2.55 to 2.64, and a shift of the luminescence spectrum toward shorter waves. No answer could be obtained concerning a change in the interatomic distances, however, because the hypothetical new HgO phase did not manifest itself in terms of new lines on the x-ray radiogram. With the x-ray dispersivities of oxygen and mercury atoms in the ratio 1 : 8, the contribution of a few displaced oxygen atoms to the total dispersion could only be slight. Much broader lines were noted on HgO diffractograms, indicating high microstresses in the lattice which could, for instance, be associated with the appearance of fragments of a new phase. Along with a broadening of diffraction lines, which was much more significant in the case of HgO than in the case of any other shock compressed test material, there occurred also a change in the integral intensity of diffraction lines. The diffractograms were taken on a model DRON-1 diffractometer with filtered radiation from a copper target. Inasmuch as a tendency to grain orientation was noted in specimens, special care was taken in their preparation: the powder was deposited through a sieve on a viscous substrate.

Since no new lines could be seen on an x-ray radiogram under unfavorable conditions of measurement, changes in the oxygen enclosure around mercury in the test substances were recorded by neutronography with a much more favorable oxygen-to-mercury dispersivity ratio (1 : 2.2). Neutronograms of the red and of the brown HgO forms are shown in Fig. 2. An additional peak at d/n = 1.92 is seen in the case of brown HgO.

If one possible phase transformation during shock compression is assumed to be the formation of fragments analogous to sphalerite (HgS), then to the new line noted on the neutronogram one may assign the indices 0.2.2 of one among the most intensive sphalerite lines. The parameter of a unit cell of the hypothetical cubic HgO form will be here a = 5.43 Å (a = 5.84 Å for HgS), and the Hg–O distance will be 2.35 Å, as compared to 2.53 Å for HgS. The values obtained for HgO and HgS are within a reasonable correspondence, inasmuch as the sulfur atom and ion radii are somewhat larger than the respective oxygen radii. The diffraction pattern calculated on the basis of a hypothetical cubic form correlates with the differences between red HgO and brown HgO neutronograms indicated by arrows in Fig. 2.

It is also interesting to note that during shock compression of hexagonal HgS there occurs a transition to cubic HgS [7].

The Hg–O interatomic distance r = 2.35 Å determined for the hypothetical cubic HgO is equal to the sum of ion radii calculated for an Hg^{2+} atom (1.06 Å) and an O^{2-} atom (1.29 Å) with corrections made to account for the coordination [2].

All these findings corroborate the hypothesis concerning the increase in the coordination number which follows an increase in the ionization of bonds and in the interatomic distances.

Thus, on the basis of the shift of the x-ray absorption limit detected in experiments and on the basis of changes in the neutronogram of HgO after shock compression, one may state hypothetically that a new HgO form is produced whose structure is of sphalerite type. It is a metastable form which appears in small quantities and possibly in dispersion, which makes its examination difficult.

NOTATION

η is the effective coordination charge [4];
ΔE is the energy shift at the L_{III} absorption limit;
d/n is the interplane distance in a crystal lattice.

LITERATURE CITED

1. S. S. Batsanov and E. D. Ruchkin, Izv. Sib. Otd. Akad. Nauk SSSR, 1, No. 2, 145 (1967).
2. S. S. Batsanov, É. M. Moroz, S. S. Derbeneva, E. V. Dulepov, A. I. Lapshin, and V. I. Alikin, Zh. Strukt. Khim., 10, No. 5, 8 (1969).
3. I. A. Ovsyannikova and S. S. Batsanov, Proceedings of the International Conference on X-ray Spectroscopy [in Russian], Part 2, Kiev (1968).
4. I. A. Ovsyannikova, S. S. Batsanov, L. I. Nasonova, L. R. Batsanova, and É. A. Nekrasova, Izv. Akad. Nauk SSSR, Ser. Fiz., 31, No. 6, 922 (1967).
5. K. Aurivillius, Acta Chem. Scand., 10, 852 (1956).
6. K. Aurivillius and I. B. Carlsson, ibid., 12, 1297 (1958).
7. V. I. Vasil'ev, Geologiya i Geofizika, No. 4, 143 (1964).
8. S. S. Batsanov, Zh. Strukt. Khim., 3, No. 5, 616 (1962).