JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 17, SUPPLEMENT B-II, 1962
PROCEEDINGS OF INTERNATIONAL CONFERENCE ON MAGNETISM AND CRYSTALLOGRAYHY, 1961, VOL. II

Neutron Diffraction Studies of Higher Carbides of Heavy Metals*

MASAO ATOJI
Chemistry Division, Argonne National Laboratory
Argonne, Illinois, U.S.A.

The neutron diffraction and paramagnetic scattering analyses of the CaC_2 type carbides (CaC_2, YC_2, LaC_2, CeC_2, TbC_2, YbC_2, LuC_2 UC_2) and the Pu_2C_3 type carbides (La_2C_3, Ce_2C_3, Pr_2C_3, Tb_2C_3) show strong correlations between the interatomic distances and the metal valency. These correlations and the vanishing Knight shift of YC_2 can reasonably be interpreted from the following postulations. The conduction band wave functions of MC_2 are composed only of the metal *d*-orbitals and the $C_2-\pi_g 2p$ antibonding orbitals. The $C_2-\pi_g 2p$ contribution to the conduction band is smaller in M_2C_3 than in MC_2. The conduction band of M_2C_3 is also associated with the metal *s*-orbital.

The crystal structures and/or chemical properties of the higher carbides of metals, M_xC_y with $x<y$, indicate that in all known higher carbides the carbon atoms are always grouped together to form C_2 or higher carbon molecules. The present paper discusses the crystal and electronic structures of the higher carbides containing the C_2 groups; MC_2-tetragonal D_{4h}^{17}-$I4/mmm$ with two chemical formulae per unit cell (M=Ca, Sr, Ba, Y, La and rare earth elements, U)[1)-6)] and M_2C_3-cubic T_d^6-I$\bar{4}$3d, with eight formulae per unit cell (M=La to Ho, U, Pu)[1),3),6)]. All but the alkaline earth metal dicarbides possess typical metallic properties.

The full-matrix least-squares analyses on the powder diffraction intensities of CaC_2, YC_2, LaC_2 CeC_2, TbC_2, YbC_2, LuC_2, UC_2, La_2C_3, Ce_2C_3, Pr_2C_3, and Tb_2C_3 yielded the C-C bond distances of 1.191±0.009, 1.275±0.002, 1.303±0.012, 1.283±0.004, 1.293±0.009, 1.287±0.010, 1.276±0.012, 1.340±0.007, 1.236±0.059, 1.276±0.005, 1.239±0.003, and 1.240±0.005Å, respectively. The neutron paramagnetic scattering analyses or the magnetic susceptibilities revealed that all metal atoms in these carbides are in their trivalent Hund ground state, except Ca (divalent), Yb in YbC_2 (possible valency of 2.8), U in UC_2 (possibly tetravalent) and Ce in Ce_2C_3 (valency of 3.4). In summary, the C-C distances in $M^{+2}C_2$, $M^{+3}C_2$, $M^{+4}C_2$, $M_2{}^{+3}C_3$, and $M_2{}^{+3.4}C_3$ are 1.191, 1.278, 1.340, 1.238, and 1.276Å, respectively. The percentage deviations from the ionic distances R_i on the shortest C-M distances R, $(R_i-R)/R_i$, is 0, 6, 10, 4, and 5%, respectively, for $M^{+2}C_2$, $M^{+3}C_2$, $M^{+4}C_2$, $M_2{}^{+3}C_3$, and $M_2{}^{+3.4}C_3$. In both MC_2 and M_2C_3, the C-C distance and also the covalent character on the C-M distance increase as the metallic valency increases. The C-C distance for YbC_2 shows no significant effect due to the anomalous valency of Yb, but the C-M distances in YbC_2 are about 3% longer than the interpolated value for $Yb^{+3}C_2$. The energy level consideration[7)] and the magnetic data[4),8)] suggest the electronic configuration of the C_2 group as $C_2{}^=$ with KK $(\sigma_g 2s)^2$ $(\sigma_u 2s)^2$ $(\pi_g 2p)^4$ $(\sigma_g 2p)^2$ in all of the MC_2 and M_2C_3 compounds.

It is therefore reasonable to assume that the metallic MC_2 compounds are composed of M^{+n}, $C_2{}^=$ and $(n-2)$ electrons. Metal orbitals, *s* and *d* (5*s* and 4*d* for Y, 6*s* and 5*d* for rare earths, 7*s* and 6*d* for U) and the $C_2{}^=$ antibonding orbitals, $\pi_g 2p$, are readily available for bonding, but the symmetries (4/*mmm* for M and 4*mm* for C) allow only d_{yz} or $d_{zx}\sim\pi_g 2p$ ($z\equiv c$ axis) combination for the molecular integrals. Since the $(n-2)$ electrons should occupy the $d\sim\pi_g 2p$ orbitals, one expects a longer C-C distance and a more covalent C-M bond for the larger n, in accordance with the observed results. The $d\sim\pi_g 2p$ combination is multiple-centered and largely delocalized. Hence, these $(n-2)$ electrons partly filling the $d\sim\pi_g 2p$ band can be considered as conduction electrons. No Knight shift was observed for the NMR spectra of YC_2[9)], supporting the present in-

---

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

terpretation.

For obtaining the largest overlapping effect between the given atomic orbitals, the molecular integral axis, x, may be chosen parallel to either $\langle 100\rangle$ or $\langle 110\rangle$ axis. The former gives a maximum electron density around a point (1/2, 0, 1/4) with $(n-2)/2$ electrons/eight centered bond and the latter, (1/4, 1/4, 1/4) with $(n-2)/4$ electrons/four centered bond. In either case, the wave function for the conduction electron has nodes at the C_2 sites, i.e. the conduction electrons are repelled by the negatively charged C_2 groups. Subsequently, one expects a vanishing Knight shift also at the carbon positions. The electrostatic potential calculations are in favor of the (1/2, 0, 1/4) model. For instance, in the case of UC_2 with U^{+4}, $C_2^{=}$ and two electrons, the potentials for U, C and electrons at the (1/2, 0, 1/4) positions are -16.566, 2.281 and 4.047 e.s.u./Å, respectively. For the model in which the electrons are at the (1/4, 1/4, 1/4) positions, the values, -17.590, 2.129 and -4.688 e.s.u./Å are obtained, respectively, for U, C and the electron. One sees that the (1/2, 0, 1/4) positions attract the electron but the (1/4, 1/4, 1/4) positions repel it. The total electrostatic energies are 2189 kcal/mol for the (1/2, 0, 1/4) model and 1810 kcal/mol for the (1/4, 1/4, 1/4) model, while the uniform charge density gives 2058 kcal/mol which lies about midway between the two models in question. Although the calculation is based on the point-charge approximation, these results seem to elucidate the (1/2, 0, 1/4) model as the most probable one. The $M^{+3}C_2$ structure gave a similar result to the UC_2 case.

In $M_2^{+3}C_3$, the symmetries (3-fold rotation for La, 2 for C and $\bar{4}$ for the mid-point of C_2) suggest, in addition to $d\sim\pi_g 2p$, considerable contribution of the metal s-orbital to the lowest conduction band. In other words, the conduction electrons in $M_2^{+3}C_3$ are associated with the metal orbitals with a higher order than those in the metallic MC_2 compounds and the reversed relation may be postulated for the $\pi_g 2p$ orbitals. In fact, the shortest M-M distances in $M_2^{+3}C_3$ are nearly 10% shorter than those in the corresponding dicarbides, while the C-M distances are comparable. The conduction electrons per C_2 group are 4/3 for $M_2^{+3}C_3$ and one for $M^{+3}C_2$. Yet the observed result that the C-C distance is shorter in $M_2^{+3}C_3$ can be explained by the lesser contribution of the C_2 antibonding orbitals to the conduction band. In Ce_2C_3, all interatomic distances except the C-C distance are considerably shorter than the interpolated values for Ce^{+3}. The Ce atoms in Ce_2C_3 may be regarded as a resonating state of $4f\ ^2F_{5/2}$ and $^1S_0$. The Knight shift should be observed for M in M_2C_3.

The effective nuclear charges, $(Z-S)$, for the $4f$ hydrogenic radial wave functions of Ce, Pr, Tb, and Yb as determined from the neutron paramagnetic scattering are 19, 19, 22, and 27, respectively. These values are approximately 20 to 30% larger than Slater's[10] and Pauling's[11] values but roughly 20% smaller than those deduced from the spectroscopic multiplet structure[12]. The screening constants may vary considerably with the property chosen to define it, especially those for the outer electrons. However, the large spread of the $(Z-S)$ values mentioned above are rather unexpected for the $4f$ electrons. This subject will be clarified after the $(Z-S)$ values, defined by and obtained from the self-consistent field treatment, become available for the rare earth atoms.

The statistical averages of the slow neutron scattering amplitudes obtained from the dicarbide data and those reported previously[13),14)] are, 0.488±0.007, 0.796±0.009, 0.832±0.014, 0.482±0.006, 0.756±0.020, 1.262±0.012, 0.73±0.02, and 0.851±0.022, all in 10^{-12} cm with positive sign, for Ca, Y, La, Ce, Tb, Yb, Lu, and U, respectively. The total nuclear scattering cross sections of Tb, Yb and Lu at 0.0735 ev were found to be 20±2, 30±3 and 13±2 barns, respectively. The coherent scattering amplitude of $_{70}Y$ is very large. Since $_{70}Y$ is composed of seven stable isotopes with a rather uniform abundant ratio, at least one of the isotopes may have an extraordinarily large scattering amplitude.

All but CaC_2 were prepared by the high-temperature direct combination of the respective metal and graphite. In most of the carbide preparations, the formation of eutectic conglomerate is unavoidable. Hence, all samples were subjected to emission spectrographic, chemical and X-ray diffraction analyses for the determination of impurities. At least two place accuracy for the impurity content was obtained by combining these analytical methods. The impurity peaks and the overlapped peaks in the powder diagram were treated with help of the least-squares method[14]. The structure analysis was based on the least-squares method for minimizing the function, $\sum_{u} W(I_{\mathrm{obs}}-I_{\mathrm{calc}})^2$, where intensities were used rather than the structure factors. The conventional agreement factors obtained from the full-matrix refinement were as small as 2% for most of the carbides.

Part of the neutron experiments were carried out at the Oak Ridge National Laboratory through the kind invitation of Dr. H. A. Levy, to whom the author is deeply indebted. The author is also grateful to Dr. H. A. Daane for providing the neutron samples and Mr. D. E. Williams for his help in the IBM 650 computation.

References

1 M. Atoji, K. Gschneidner, Jr., A. H. Daane, R. E. Rundle, and F. H. Spedding: J. Am. Chem. Soc. **80** (1958) 1804.
2 M. Atoji and R. C. Medrud: J. Chem. Phys. **31** (1959) 332.
3 F. H. Spedding, K. Gschneider, Jr., and A. H. Daane: J. Am. Chem. Soc. **80** (1958) 4499.
4 R. C. Vickery, R. Sedlacek and A. Ruben: J. Chem. Soc. **103** (1959) 498 and **104** (1959) 503.
5 F. H. Spedding, K. Gschneidner, Jr. and A. H. Daane: AIME Trans. **215** (1959) 192.
6 W. B. Wilson: J. Am. Ceramic Soc. **43** (1960) 77.
7 E. Clementi and K. S. Pitzer: J. Chem. Phys. **32** (1960) 656.
8 M. Atoji: J. Chem. Phys. **35** (1961) 1950.
9 R. G. Barnes and W. H. Jones, Jr.: Private communication.
10 J. C. Slater: Phys. Rev. **36** (1930) 57.
11 L. Pauling and J. Sherman: Z. Krist. **81** (1932) 1.
12 P. F. A. Klinkenberg: Physica, **13** (1947) 1.
13 D. J. Hughes and R. B. Schwartz: *Neutron Cross Sections* (U. S. Government Printing Office, Washington, D. C., 1958).
14 M. Atoji: Phys. Rev. **121** (1961) 610.