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# Anharmonic oscillations of nuclei.

By James A. Ibers, *Shell Development Company, Emeryville, California, U.S.A.*

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The measures of internuclear distances that are of theoretical interest, and which provide a basis for intercomparisons of the results of different physical measurements, are, of course, $r_e$, the equilibrium distances corresponding to the minima on the potential energy hypersurface of the molecule. In diffraction studies a determination of time-average distances, $r$, rather than of $r_e$, is usually made. This is understandable for the distances determined, being complex functions of the thermal motions of the nuclei, are difficult to relate to equilibrium distances, and, moreover, at least in X-ray and electron diffraction studies the differences between $r$ and $r_e$ are less than the experimental uncertainties in $r$.* The differences between $r$ and $r_e$ are greatest for those distances involving the lightest nuclei, and for the determination of such distances, partly because of the weak and uncertain nature of the scattering from light atoms, the X-ray and electron diffraction methods have not been too effective. On the other hand, the neutron diffraction method is now employed to yield internuclear distances involving the lightest nuclei to a much greater accuracy, and here the distinction between $r$ and $r_e$ may be important. In fact it is the purpose of this note to suggest, by way of an idealized model, that the usual failure in current neutron diffraction studies to take into account the anharmonic† nature of thermal oscillations of nuclei may result in differences between $r$ and $r_e$ of the order of magnitude of the limits of error assigned to $r$.

Consider a bond $M$–$H$, and assume that $M$ is much heavier than $H$. If the hydrogen nucleus vibrates harmonically in the direction of the bond with a frequency $\nu$, then the probability of finding it at a distance $r$ from $M$ is in the lowest vibrational state

$$P(r-r_e) = (\alpha/\pi)^{\frac{1}{2}} \exp\left[-\alpha(r-r_e)^2\right], \qquad (1)$$

where $\alpha$, the harmonic oscillator function, is

$$\alpha = 4\pi^2 m\nu c/h . \qquad (2)$$

Hence, the most probable position for the hydrogen nucleus is at $r = r_e$. But suppose that the hydrogen nucleus vibrates anharmonically in the direction of the bond. If one assumes the Morse potential function (Morse, 1929) with anharmonicity coefficient $x_e$ (in the quadratic in $(v+\frac{1}{2})$ expression for the vibrational energy levels) then in the lowest vibrational state one finds

$$P(Z) = (2x_e\alpha)^{\frac{1}{2}}[\Gamma(x_e^{-1}-1)]^{-1}\, e^{-Z} Z^{(1-x_e)/x_e} , \qquad (3)$$

where

$$Z = x_e^{-1} \exp\left[-(2x_e\alpha)^{\frac{1}{2}}(r-r_e)\right] . \qquad (4)$$

Note that the position of maximum probability for the hydrogen nucleus satisfies the condition

$$\exp\left[-(2x_e\alpha)^{\frac{1}{2}}(r-r_e)\right] = 1-x_e , \qquad (5)$$

which for $x_e$ small leads to

$$r-r_e \approx (x_e/2\alpha)^{\frac{1}{2}} . \qquad (6)$$

Hence on an ideal Fourier map, free from all spurious effects, the position of the hydrogen nucleus, as judged by the position of maximum scattering density, would correspond to a distance $r$, rather than to a distance $r_e$, away from $M$. The difference between $r$ and $r_e$ is difficult to calculate owing to the paucity of spectroscopic data from solids and to the difficulties inherent in the interpretation of such data. On the other hand values of $x_e$ for gases can be estimated by various methods (e.g., Dennison, 1940), and typical values are perhaps 0·02 to 0·10 (Redlich, 1939; Dennison, 1940). If one assumes that the isotope product rule is applicable to solids, then the data of Lord & Merrifield (1953) for $\nu(H)$ and $\nu(D)$ in several solids lead to values of $x_e$ around 0·2. It is thus not unreasonable to assume that $x_e$ values found for gases obtain also in solids, and a conservative value of 0·05 for $x_e$ can be taken here. A typical value of $\alpha$ is about 80 Å$^{-2}$. Hence, the difference between $r$ and $r_e$ is about 0·02 Å for the ground vibrational state, approximately the magnitude of the limits of error in neutron diffraction determinations of bond distances involving hydrogen atoms. This difference would be expected to be greater in some cases, for example for the hydrogen atom in a short O–H–O bond where $x_e$ should be somewhat larger. It is interesting to note that if a Fourier peak, such as Bacon & Pease (1955) find for the hydrogen atom in the short O–H–O bond in $KH_2PO_4$, can be decomposed into two half-hydrogen peaks of Gaussian shape ($x_e = 0$) separated by $\delta$, then it can be decomposed equally well into two half-hydrogen anharmonic peaks separated by $\delta+(2x_e/\alpha)^{\frac{1}{2}}$.

The effects of such anharmonicities on the actual determinations of bond distances by neutron diffraction techniques are quite difficult to estimate. Such determinations, which invariably assume the vibrations to be harmonic, are generally carried out either by least-squares or difference Fourier techniques. In either case the bond distances derived are rather complicated and to some extent uncertain functions of the thermal motions (Worsham, Levy & Peterson, 1957). Thus deviations from harmonicity would take a far more subtle form than on the ideal Fourier map discussed above. It is reasonably certain, however, that the errors introduced by neglect of anharmonicity are small, but are perhaps comparable to the estimated limits of error of such neutron diffraction studies. Anharmonicity of thermal oscillations will undoubtedly have to be taken into account as part of a more sophisticated treatment of thermal oscillations in diffraction studies, and such a treatment is needed if the neutron diffraction method is to yield equilibrium bond distances involving the lighter nuclei to greater accuracy than is possible at present.

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* However, should the reliability of such experimental values of $r$ increase sufficiently, then for purposes of comparison with theory it will be necessary to know how to relate $r$ to $r_e$.

† In practice the anharmonic nature of thermal oscillations is associated with asymmetry in the potential function describing such motion, and accordingly we use the term anharmonic to imply such asymmetry. The rare, if not idealized, case of the anharmonic oscillator with symmetric potential function is of no interest to us.

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## Isotypie zwischen Pharmakosiderit und zeolithischen Germanaten.

Von J. Zemann, *Mineralogisch-kristallographisches Institut der Universität, Göttingen, Deutschland*

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Neben den silikatischen Zeolithen gibt es auch noch einige andere anorganische Verbindungen mit analogen Eigenschaften. Zu diesen gehört das kubische Mineral Pharmakosiderit, $KFe_4(AsO_4)_3(OH)_4 . 6–8\ H_2O$, dessen Kristallstruktur im Prinzip geklärt ist (Zemann, 1947*a*, 1947*b*, 1948). Strukturbestimmend ist ein Gerüst $^3_\infty[Fe_4^{[6]}(AsO_4)_3(OH)_4]^{1-}$, in welchem jeder Sauerstoff zu einem $AsO_4$-Tetraeder und einem $FeO_3(OH)_3$-Oktaeder gehört, jede Hydroxylgruppe aber zu drei $FeO_3(OH)_3$-Oktaedern. In den weiten Kanälen der Struktur sitzen die Wassermoleküle und Kaliumionen in lockerer Bindung. Einen isotypen Alumopharmakosiderit haben Hägele & Machatschki (1937) synthetisiert.

Einige Jahre später haben unabhängig davon Nowotny & Wittmann (1953, 1954, 1956, 1957) eine Strukturbestimmung an zeolithischen Alkaligermanaten durchgeführt. Die Parameter wurden für $Li_3HGe_7O_{16} . 4\ H_2O$ bestimmt. Die gefundene Struktur entspricht weitgehend dem Pharmakosiderit. Das Gerüst hat hier den kristallchemischen Aufbau $^3_\infty[HGe_4^{[6]}(Ge^{[4]}O_4)_3O_4]^{3-}$; die Füllung der Kanäle ist etwas anders als bei Pharmakosiderit, was bei zeolithartigen Verbindungen aber nicht sehr auffällig ist. Die Lage der Wasserstoffatome konnte in beiden Fällen nur vermutet werden. Tabelle 1 gibt den Vergleich der Gerüste der beiden Substanzen nach Transformation auf dasselbe Koordinatensystem.

Damit scheint es gerechtfertigt, diese bisher getrennt beschriebenen Zeolithe wegen des geometrisch identen Gerüstes zu einem gemeinsamen 'Pharmakosiderit-Typ' zusammen zu fassen. In Tabelle 2 sind die bisher bekannten Vertreter angeführt. Vermutlich wird man für diesen Strukturtyp noch weitere Beispiele finden.

Tabelle 2. *Vertreter des Pharmakosiderit-Typs*

| Formel | Gitterkonstante |
|---|---|
| $KFe_4(AsO_4)_3(OH)_4 . 6–8\ H_2O$ | 7,91 kX. |
| $KAl_4(AsO_4)_3(OH)_4 . 6–8\ H_2O$ | 7,72 |
| $Li_3HGe_7O_{16} . 4\ H_2O$ | 7,66 |
| $Na_3HGe_7O_{16} . 4\ H_2O$ | 7,67 |
| $K_3HGe_7O_{16} . 4\ H_2O$ | 7,68 |
| $(NH_4)_3HGe_7O_{16} . 4\ H_2O$ | 7,70 |
| $Rb_3HGe_7O_{16} . 4\ H_2O$ | 7,71 |
| $Cs_3HGe_7O_{16} . 4\ H_2O$ | 7,73 |
| $Ag_3HGe_7O_{16} . 4\ H_2O$ | 7,65 |
| $Tl_3HGe_7O_{16} . 4\ H_2O$ | 7,68 |

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Tabelle 1. *Vergleich der Strukturgerüste von Pharmakosiderit und zeolithischem Lithiumgermanat*

| | Pharmakosiderit | Zeolith. Lithiumgermanat |
|---|---|---|
| Formel | $KFe_4(AsO_4)_3(OH)_4 . 6–8\ H_2O$ | $Li_3HGe_7O_{16} . 4\ H_2O$ |
| Gitterkonstante $a$ | 7,91 kX. | 7,66 kX. |
| Raumgruppe | $P\bar{4}3m$ | $P\bar{4}3m$ |
| 3 As bzw. 3 Ge auf $3(d)$ | $\frac{1}{2}, 0, 0$ usw. | $\frac{1}{2}, 0, 0$ usw. |
| 4 Fe bzw. 4 Ge auf $4(e)$ | $x, x, x$ usw.<br>$x = 0{,}13_1$ | $x, x, x$ usw.<br>$x = 0{,}135–0{,}140$ |
| 12 O auf $12(i)$ | $x, x, z$ usw.<br>$x = 0{,}12_5,\ z = 0{,}37_5$ | $x, x, z$ usw.<br>$x = 0{,}11,\ z = 0{,}36$ |
| 4 OH bzw. 4 O auf $4(e)$ | $x, x, x$ usw.<br>$x = 0{,}87_5$ | $x, x, x$ usw.<br>$x = 0{,}87$ |