Dynamical Quadrupole Interactions in the Hafnium Deuterium System *

M. Forker, L. Freise, and D. Simon
Institut für Strahlen- und Kernphysik der Universität Bonn

H. Saitovitch and P. R. J. Silva
Centro Brasileiro de Pesquisas Fisicas, Rua Xavier Sigaud 150, Rio de Janeiro, Brazil

Z. Naturforsch. **41 a,** 403–407 (1986); received July 22, 1985

The nuclear quadrupole interaction (NQI) at the site of ^{181}Ta in HfD_2 has been investigated by time differential perturbed angular correlation measurements. Below 290 K the NQI is static within a 300 nanosecond time window. Above 290 K dynamic effects related to the diffusion of deuterium atoms start to appear, which have been analyzed in terms of a 3-state stochastic model. Between 345 K and 500 K the jump diffusion of deuterium has an activation energy $E_a = (0.33^{+0.9}_{-0.4})$ eV. At higher temperatures the relaxation spectra suggest that transitions occur, first to the δ-phase, then to the α-phase of the hafnium-deuterium system. At 600 K the mean residence time between jumps is of the order of 2 nanoseconds. First measurements with HfH_2 show an isotope effect compatible with the prediction of the classical rate theory for over-barrier diffusion.

Introduction

Atomic motion in solids gives rise to fluctuating electric field gradients (EFG), and as a consequence probe nuclei with finite electric quadrupole moments experience a time dependent nuclear quadrupole interaction (NQI). One of the experimental methods for the investigation of dynamical NQI is the time differential perturbed angular correlation (TDPAC) technique, which detects the spin relaxation caused by a time dependent interaction in an ensemble of aligned nuclear spins [1].

We are presently employing the TDPAC technique to study the motion of hydrogen atoms in the various phases of the hafnium-hydrogen (Hf-H) system, using ^{181}Ta, which is populated in the decay of radioactive ^{181}Hf, as nuclear probe. HfH_2, HfD_2 and $HfH_{1.72}$ have been studied, but the data treatment has been completed only for hafnium deuteride HfD_2. The results obtained for HfD_2 are presented in this paper.

At room temperature the Hf-H systems exhibits 3 stable phases [2]: Hydrogen dissolved in hcp Hf metal forms the α-phase with a maximum H concentration of less than 1 at% at room temperature. The δ-phase is a fcc structure with H concentrations between 63 and 64.3 at% ($HfH_{1.70}$ and $HfH_{1.80}$), and the ε-phase extends from $HfH_{1.87}$ to $HfH_{1.99}$. In the following we shall refer to the ε-phase as to hafnium dihydride HfH_2, regardless of the actual H concentration. Hafnium dihydride forms a distorted CaF_2 structure, in which the hydrogen atoms occupy tetrahedral sites of the hafnium face centered tetragonal lattice which is contracted along the c-axis [3]. Substitution of deuterium for hydrogen in HfH_2 results in slightly shortened bonds and a stronger contraction [4].

Experimental Details

The TDPAC measurements were carried out with 4-detector arrangements such as described in [5]. HfD_2, commercially available from Ventron Corporation, was neutron irradiated to produce ^{181}Hf nuclei which by β-decay feed the 133–483 keV cascade of ^{181}Ta. The time spectra of the angular correlation coefficients A_{22} and A_{44} were measured at different source temperatures between 19 K and

---

* Presented at the VIIIth International Symposium on Nuclear Quadrupole Resonance Spectroscopy, Darmstadt, July 22–26, 1985.

Reprint requests to Dr. M. Forker, Institut für Strahlen- und Kernphysik der Universität Bonn, Nussallee 14–16, D-5300 Bonn.

0340-4811 / 86 / 0100-0403 $ 01.30/0. – Please order a reprint rather than making your own copy.

Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition “no derivative works”). This is to allow reuse in the area of future scientific usage.

1000 K in a vacuum of 10^{-5} Torr. The X-ray diffraction analysis of the compound at room temperature confirmed a pure ε-phase HfD_x with $x > 1.87$. The exact deuterium concentration within the ε-phase was not determined.

When HfD_2 is heated in vacuum, deuterium losses and phase transformations will occur at certain temperatures. We have tried to study the stability range of the ε-phase by taking a room temperature (RT) TDPAC spectrum after each increase of the sample temperature. First irreversible changes in the RT spectrum were observed after heating the compound above 750 K: Static NQI frequencies corresponding to the NQI in Hf metal started to appear in the RT spectrum, while the spectrum at 750 K still showed relaxation effects. In the X-ray analysis of a sample heated to 770 K for 24 hours only the reflexes of Hf metal were found. Apparently, at about 750 K HfD_2 transforms to the α-phase with some deuterium dissolved in hcp Hf metal, producing relaxation effects at elevated temperatures. After heating the compound above 900 K the deuterium is completely expelled and now the TDPAC spectrum both at 900 K and RT contains only the static NQI frequency ($\nu_Q = 330$ MHz at 290 K) corresponding to metallic Hf.

As only the transition to the low concentration α-phase has been detected, the RT TDPAC spectra in the ε- and in the intermediate δ-phase are probably very similar. This would imply that the static NQI seen by the probe nuclei at RT is rather insensitive to changes of the deuterium concentration. For more information on this aspect we are preparing simultaneous TDPAC and X-ray diffraction measurements with samples previously heated to different temperatures.

Results

Figure 1 shows the TDPAC spectra $A_{22}G_{22}(t)$ in the reversible temperature range between 19 K and 700 K. There are pronounced changes as temperature is increased.

Between 19 K and 290 K one observes a TDPAC spectrum characteristic for a large distribution of time independent NQI's. Typical for such spectra is the 'hard core' value $G_{22}(\infty) = 0.2$ at large delay times [1]. A fit of the theoretical perturbation factor $G_{22}(t)$ for a static NQI with a Gaussian distribution of relative width δ [1] gives identical results for 19 K and 290 K: The center frequency of the distribution is $\nu_Q = e\,Q\,V_{zz}/h = 260(10)$ MHz, the relative width $\delta = 0.28(2)$ and the asymmetry parameter of the EFG is $\eta = (V_{xx} - V_{yy})/V_{zz} = 0.49(2)$. With $Q =$ 2.51 b for the quadrupole moment of the 5/2 state of ^{181}Ta, the NQI frequency corresponds to an EFG of $V_{zz} = 4.3 \cdot 10^{17}$ V/cm^2. The observation of a broad frequency distribution and an axial asymmetry in an axially symmetric lattice such as stoichiometric HfD_2 is usually attributed to lattice imperfections, strains and impurities [6]. In the present case vacancies probably play a dominant role. The deuterium concentration of the ε-phase is usually smaller than for perfect stoichiometry and one has vacancies in the D sublattice. As the Hf-D distance (2.05 Å) is much smaller than the Hf-Hf distances (3.28, 3.47 Å) the EFG at the probe site is mainly determined by the D environment. Therefore a vacancy in the tetragonal deuterium lattice lowers the symmetry of the interaction and different vacancy configurations in near neighbor shells give rise to large EFG distributions.

Above 300 K the TDPAC spectra begin to change with increasing temperature. The anisotropy at delay times larger than 15 nsec decreases below the 'hard core' value $G_{22}(\infty)$ for static NQI, indicating the onset of atomic motion on a time scale comparable to the life time of the 5/2 state of ^{181}Ta (15 nsec): Deuterium atoms move most probably along tetrahedral sites, producing a fluctuating NQI. At about 500 K the destruction of the anisotropy at large times is complete: the anisotropy drops to zero within a few nanoseconds without any recovery at larger times. Between 500 K and 534 K the spectra remain unchanged. At about 550 K the initial decrease starts to be slower, and as temperature is raised one observes an increasing recovery of the anisotropy at larger times. Above 600 K the TDPAC spectra are well described by single exponential functions $G_{kk}(t) = \exp(-\lambda_k t)$, with the decay constants λ_k decreasing with increasing temperatures [7].

The various approaches to treat the effect of dynamic interactions on angular correlations have been recently reviewed by Dattagupta [8]. Here we are dealing with a diffusion process where vacancies jump between the sites of the D sublattice, producing an axially asymmetric fluctuating EFG. Blume's stochastic model [9] and also the model of

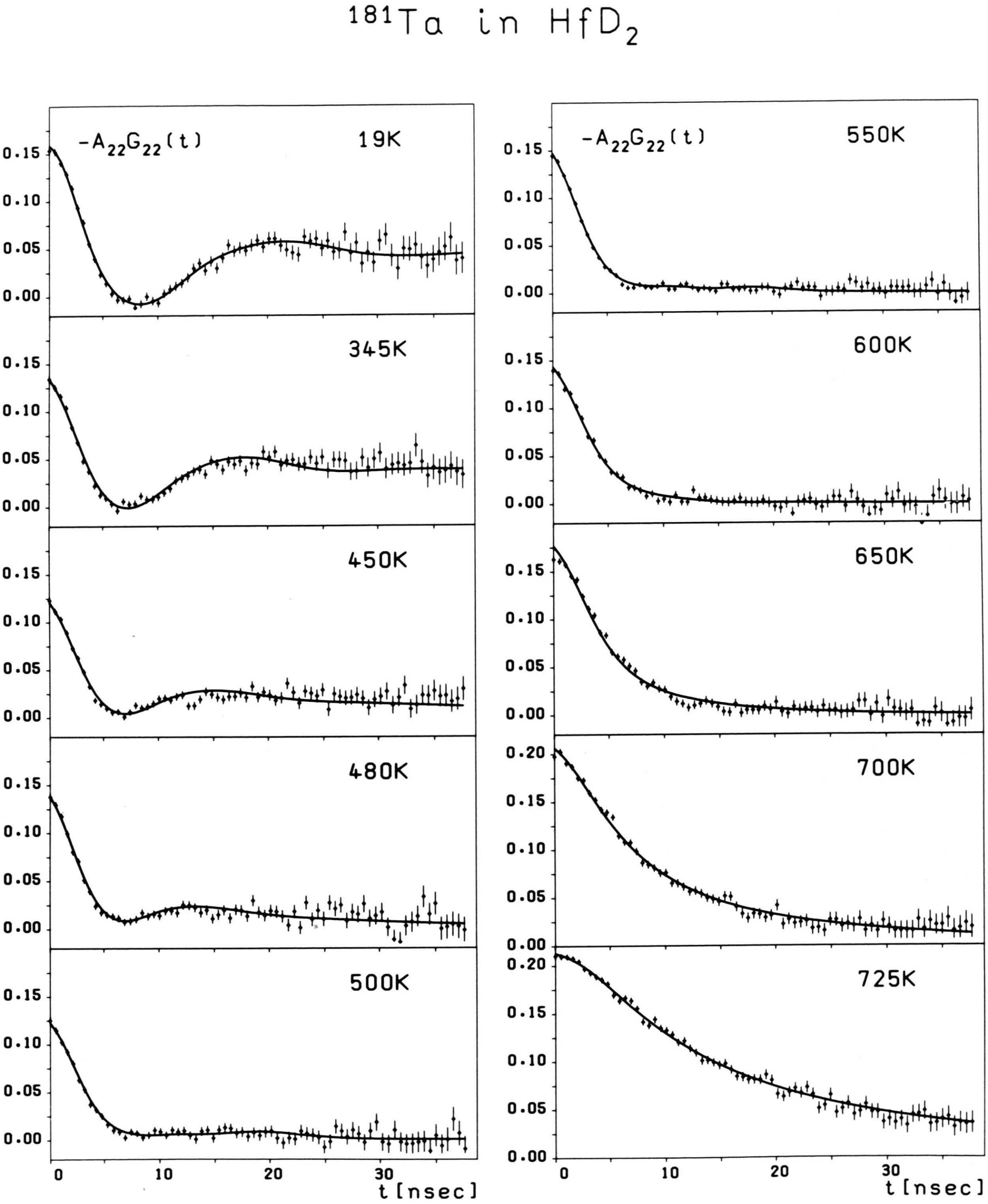

Fig. 1. TDPAC spectra of ^{181}Ta in HfD$_2$.

random reorientation [10] could be used for a description of this situation. By comparing the stochastic model and the reorientation model in the diffusion and the strong collision limits, Winkler [10] has shown that the TDPAC spectrum is rather insensitive to the reorientation mechanism or the number of stochastic states. It is the jump frequency and hyperfine interaction (hfi) of the ensemble average which mainly determine the shape of the spectrum. It can be shown, that the restoration of the anisotropy towards the unperturbed value in the presence of strong, rapidly fluctuating hfi's is only possible, if the hfi of the ensemble average vanishes [8]. We observe such a recovery at high temperatures. We therefore analyzed our data with the simplest stochastic model compatible with axial asymmetry of the EFG and an isotropic ensemble average by assuming that the largest component of an axially asymmetric EFG jumps at random between the 3 axes of the coordinate system [11]. The solid lines in Fig. 1 are fits of this model to the data. Details of the analysis will be discussed in a forthcoming paper.

The analysis revealed a strong correlation between the quadrupole frequency and the total number of jumps per second W such that the product $\omega_Q^2 \tau$ is a constant for a given spectrum ($\omega_Q = 2\pi \nu_0 / 4I(2I-1)$), where $\tau = 1/W$ is the average residence time between jumps, if the jumping time itself is neglected. The correlation between ω_Q and τ is the stronger, the more the shape of the spectrum approaches a single exponential function, in agreement with the Abragam and Pound limit [7] for rapid isotropic fluctuations. For temperatures below 480 K ω_Q and τ can still be determined independent of each other. Up to 480 K one has $\omega_Q \simeq 50$ MHz.

In Fig. 2 we have plotted the quantity $\omega_Q^2 \tau$ as a function of the inverse temperature $1/T$. $\omega_Q^2 \tau$ decreases by nearly 3 orders of magnitude between 345 K and 725 K. Assuming $\omega_Q \simeq 50$ MHz for all temperatures, this corresponds to a decrease of the mean residence time from $\tau = 160$ nsec at 345 K to $\tau = 0.25$ nsec at 725 K. From the proton spin lattice relaxation time T_1 in the corresponding Hf dihydride $HfH_{1.96}$ [12] one estimates a proton residence time of the order of 2.5 nsec at 670 K. Because of the model dependence of this estimate [13], the accuracy is not sufficient to reveal the isotope effect, but the order of magnitude agreement with our result is very good.

Three temperature ranges may be distinguished in Figure 2:

(i) Between 345 and 480 K the quantity $\ln(\omega_Q^2 \tau)$ is in a good approximation a linear function of the inverse temperature $1/T$, suggesting an Arrhenius relation $\omega_Q^2 \tau \simeq \exp\{E_a/kT\}$ with an activation energy of $E_a = (0.33^{+0.9}_{-0.4})$ eV. The activation energies for proton jumps in the isomorphous dihydrides $HfH_{1.96}$ [12] and $ZrH_{1.98}$ [12, 14] have been investigated by pulsed NMR: $E_a = 0.55 - 0.65$ eV for $HfH_{1.96}$ and 0.83 eV for $ZrH_{1.98}$. $ZrH_{1.97}$ has also been studied by TDPAC with ^{181}Ta as probe between 20 and 588 K [15]. In contrast to our observation of a dynamic NQI in HfD_2, the spectra in $ZrH_{1.97}$ are well described by a static interaction. The proton residence time in $ZrH_{1.98}$ has been determined by Doolan et al. [14] to be of the order of 2.5 nsec at 850 K. From this value and the activation energy $E_a = 0.83$ eV one estimates that at 588 K the time between proton jumps should be of the order of 300 nsec, which is too long to be detected with the ^{181}Ta time window. For TDPAC studies of dynamic NQI in ZrH_2 the measurements should be extended to higher temperatures.

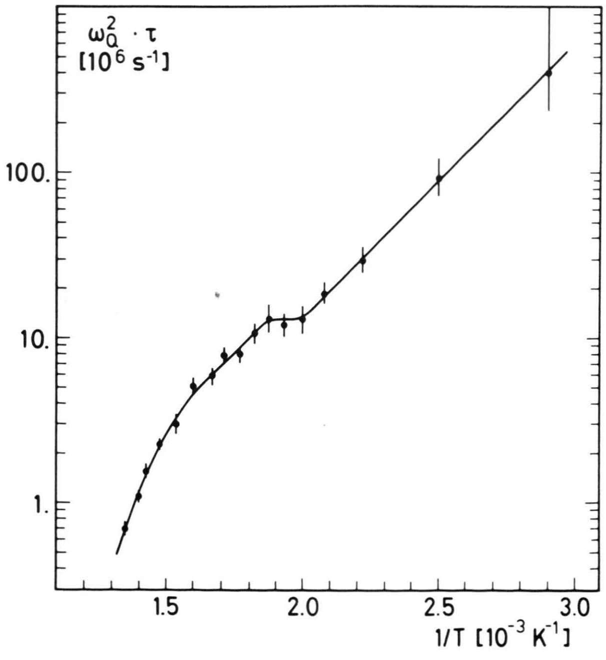

Fig. 2. The product $\omega_Q^2 \tau$ In HfD_2 vs. $1/T$. ω_Q is the quadrupole frequency $\omega_Q = 2\pi \nu_Q / 4I(2I-1)$.

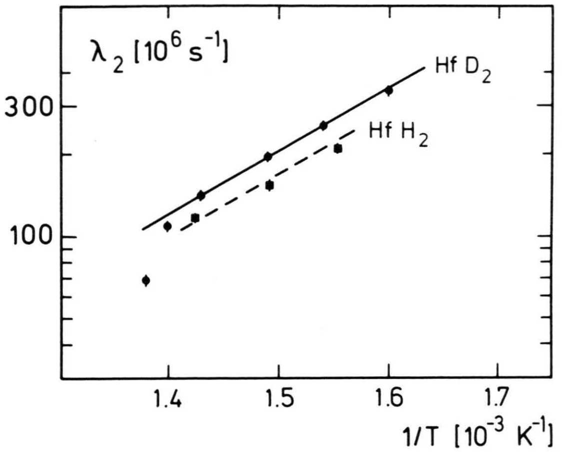

Fig. 3. The Abragam and Pound attenuation parameter λ_2 in HfD_2 and HfH_2 vs. $1/T$.

(ii) Between 500 and 550 K in $\omega_Q^2 \tau$ does not change with temperature. The reasons for this behaviour are not clear. Possibly a structure change occurs in this temperature range. This is suggested by the observation that at higher temperatures the anisotropy is restaured towards the unperturbed value. This requires fluctuations with a vanishing ensemble average. Because of the tetragonal structure of the ε-phase, however, no jump mechanism with vanishing average can be conceived for HfD_2. Therefore at some intermediate temperature a transition must occur to a cubic lattice, where the ensemble average can be zero. The δ-phase $HfD_{1.7}-HfD_{1.8}$ with its fcc lattice is an obvious candidate. To test this hypothesis X-ray studies in this temperature range would be helpful.

(iii) Above 550 K, $\ln(\omega_Q^2 \tau)$ continues to decrease with $1/T$, first with the same slope as above 480 K, but as one approaches 750 K, the decrease becomes much stronger than linear. The X-ray studies have shown that at 750 K the transition to the α-phase is complete. Therefore the strong decrease of $\omega_Q^2 \tau$ and thus the residence time between 600 K and 725 K probably reflects the increasing number of vacancies which become available for jumps as deuterium is expelled and the sample transforms more and more from the δ- to the α-phase.

At temperatures above 675 K the values of $\omega_Q^2 \tau$ from the 3-state stochastic model agree with the value obtained from a fit of the Abragam and Pound (AP) perturbation function $G_{kk}(t) = e^{-\lambda_k t}$ for rapid isotropic fluctuations with:

$$\lambda_k = 3/5\, k\,(k+1)\,(4I+1) - k\,(k+1) - 1)\,\omega_Q^2 \tau .$$

The ratio $\lambda_4/\lambda_2 \simeq 1.7$ is in agreement with the AP theorie for dynamic NQI [7].

In Fig. 3 HfD_2 is compared with first results for HfH_2 in the high temperature region. The AP attenuation parameter λ_2 is plotted vs. $1/T$. The slope of $\ln \lambda_2$ vs. $1/T$ is approximately the same in both compounds. The magnitude of the attenuation parameter shows a definite isotope effect. The ratio $\lambda_2^D/\lambda_2^H = 1.26(15)$ at 675 K is compatible with the prediction $\tau_D/\tau_H = (M_D/M_H)^{1/2}$ of the classical rate theory for over barrier diffusion.

Acknowledgements

The authors are indebted to Dr. H. Winkler for helpful advice on the problems of time dependent perturbations. The help of the Mineralogisches Institut der Universität Bonn in the X-ray studies is gratefully acknowledged. This work has been supported by the Bundesministerium für Forschung und Technologie, the 'Kernforschungsanlage' Jülich and the Conselho Nacional de Desenvolvimento Scientifico e Technologico (CNPq), Brazil.

[1] M. Forker and R. J. Vianden, Magn. Res. Rev. **7,** 275 (1983).
[2] R. K. Edwards and E. Veleckis, J. Phys. Chem. **66,** 1659 (1962).
[3] S. S. Sidhu and J. C. McGuire, J. Appl. Phys. **23,** 1257 (1953).
[4] S. S. Sidhu, J. Chem. Phys. **22,** 1062 (1954).
[5] H. F. Wagner and M. Forker, Nucl. Instrum. Methods **69,** 197 (1969).
[6] M. Forker, Nucl. Instrum. Methods **160,** 121 (1973).
[7] A. Abragam and R. V. Pound, Phys. Rev. **92,** 943 (1953).
[8] S. Dattagupta, Hyperfine Interactions **11,** 77 (1981).
[9] M. Blume, Phys. Rev. **174,** 351 (1968).
[10] H. Winkler, Z. Physik **A 276,** 225 (1976).
[11] H. Winkler and E. Gerdau, Z. Physik **262,** 363 (1973).
[12] J. M. Pope, P. P. Narang, and K. R. Doolan, J. Phys. Chem. Solids **42,** 519 (1981).
[13] W. A. Barton and C. A. Sholl, J. Phys. C **9,** 4315 (1976).
[14] K. R. Doolan, P. P. Narang, and J. M. Pope, J. Phys. F **10,** 2073 (1980).
[15] R. L. Rasera, G. K. Shenoy, B. D. Dunlap, and D. G. Westlake, J. Phys. Chem. Solids **40,** 75 (1979).