PHYSICAL REVIEW B VOLUME 33, NUMBER 6 15 MARCH 1986

Quadrupole interactions in graphite—hafnium chloride

P. W. Martin and S. R. Dong
Department of Physics, University of British Columbia, Vancouver Canada, V6T 2A6

J. G. Hooley
Department of Chemistry, University of British Columbia, Vancouver, Canada, V6T 1Y6

(Received 17 December 1984)

The intercalation of graphite by hafnium chloride has been investigated by time-differential perturbed angular-correlation measurements of the (133—482)-keV γ-γ cascade in ^{181}Ta. Electric-quadrupole interaction parameters were determined for samples prepared both by the two-zone vapor-transport technique and from solution in $SOCl_2$. In the former case the presence of chlorine is shown to be necessary for intercalation to take place and the data are fitted with the combination of a static electric-quadrupole plus time-dependent interaction. When solvent is used for the preparation a more complex spectrum is obtained, requiring an additional static interaction to obtain a reasonable fit.

I. INTRODUCTION

Although graphite-metal halides comprise the most numerous group of intercalation compounds, little information is available on group-IV*b* systems.[1,2] In the case of graphite-$HfCl_4$, the early work of Croft[3] reported that in the absence of chlorine only approximately 2% of $HfCl_4$ reacted with the graphite. The importance of the role of chlorine in the preparation of most graphite-metal chlorides has been established by several authors, while in other cases where chlorine is apparently not required it is supplied indirectly by decomposition of the intercalants during the reaction process.[2] The review article by Stumpp[1] reports the unpublished data of Frey in which stage-3 compounds of graphite-$HfCl_4$ were prepared both by the vapor-transport technique in an atmosphere of chlorine and from solution in $SOCl_2$. In the former mode of preparation, however, a chlorine pressure of 2 atm[4] was required to achieve the composition $C_{45.7}HfCl_{4.77}$, constituting a stage-3 system with a repeat distance along the *c* axis for the intercalant of 15.87 Å.

The technique of time-differential perturbed angular correlations (TDPAC) of γ rays was first applied to the study of graphite intercalation compounds (GIC's) to characterize sites in graphite-$InCl_3$.[5] Here we report TDPAC measurements on graphite-$HfCl_4$ prepared both by vapor-transport and solvent techniques.

II. THEORETICAL BACKGROUND

The theory of perturbed angular correlations of γ rays is well established and a comprehensive review can be found in the article by Frauenfelder and Steffen.[6] The 42.5-day ^{181}Hf nucleus decays predominantly by β emission to the 615-keV level in ^{181}Ta ($I=+\frac{1}{2}$). The relatively long lifetime of this state (17.6 μs) ensures that electronic equilibrium can be established prior to the subsequent (133—482)-keV γ-γ cascade in ^{181}Ta via the $+\frac{5}{2}$ intermediate state with a half-life of 10.8 ns. It is the interaction of the quadrupole moment of this state ($Q=2.5$ barns) with the local electric field gradient produced by the atomic environment that results in the perturbation of the angular correlation between the 133- and 482-keV γ rays. The latter is given to second-order approximation by

$$W(\theta,t)=e^{-t/\tau}[1+A_2G_{22}(t)P_2(\cos\theta)] ,$$

where τ is the intermediate-state lifetime, A_2 is determined by the spins and multipolarities of the transitions, and $G_{22}(t)$, the perturbation factor, contains the information of interest relating to the quadrupole interactions. For a randomly oriented ensemble of nuclei subjected to a static quadrupole interaction, this can be written

$$G_{22}(t)=s_0(\eta)+\sum_n s_n(\eta)\cos(\omega_n t) , \quad (1)$$

where $\omega_n(\eta)$ are the quadrupole frequencies, $\eta=(V_{xx}-V_{yy})/V_{zz}$ is the asymmetry parameter, and $s_n(\eta)$ are calculable coefficients. For axial symmetry ($\eta=0$) in the electric field gradient (EFG) the quadrupole splitting of the $I=\frac{5}{2}$ state gives rise to a simple harmonic series for ω_n, with $\omega_n=n\omega_0$ ($n=1,2,3$), where ω_0 is the lowest observable interaction frequency; for the case of nonaxial symmetry ($\eta\neq0$) explicit expressions for $\omega_n(\eta)$ have been given by Gerdau *et al.*[7] in terms of $\nu_q=eQV_{zz}/h$, while the method of Prestwich *et al.*[8] was used to determine the $s_n(\eta)$ coefficients.

III. EXPERIMENTAL PROCEDURE

A. Sample preparation

Graphite was exposed to the intercalant in a device that could itself be transferred to the spectrometer for measurement and later returned to the intercalant system for further treatment. During a measurement, it was of course essential that nonintercalated vapor or solution be removed from the vicinity of the intercalation compound

©1986 The American Physical Society

so that its activity would not be detected by the spectrometer. All operations were performed in a vacuum system to ensure the absence of air and moisture. The following experimental details apply to the optimum sample shape of a cylinder of diameter and height about 6 mm. The various graphites used are described in Sec. IV and the Hf foil contained ^{181}Hf produced by neutron irradiation at the McMaster University Nuclear Reactor Facility.

1. Preparation from $HfCl_4$ vapor

On the left-hand side of Fig. 1, the "jog" tube containing the Hf foil was first sealed to the vacuum system above it and then to the 7-mm outer-diameter tube below it containing the weighed graphite. The unit was then evacuated to 1 μm and flamed to remove adsorbed water vapor before dry Cl_2 was admitted to a pressure of 200 mm. The Hf was gently heated to convert it to $HfCl_4$ which stays in the jog rather than subliming onto the graphite. When conversion was complete, the Cl_2 pressure was adjusted to 450 mm or, in one run, to zero. The tube was then sealed off to a total length of 30 cm and placed in a vertical gradient furnace which maintained the graphite end at 300 °C and the top end at a lower temperature—usually 290 °C. After 24 h the tube was removed, top end first and slowly enough so that the $HfCl_4$ solid that forms on cooling would condense only in or above the jog rather than on the graphite compound that had formed at the bottom end. The tube could then be placed in the PAC detection unit. However, the upper portion of the tube containing the active $HfCl_4$ solid had to be shielded from the detection unit or completely removed by sealing it off with a torch about 6 cm above the sample. Finally, when all measurements were completed, the tube was cracked open in order to weigh the compound. From this weight and the known weight of graphite a formula C_xHfCl_4 was calculated.

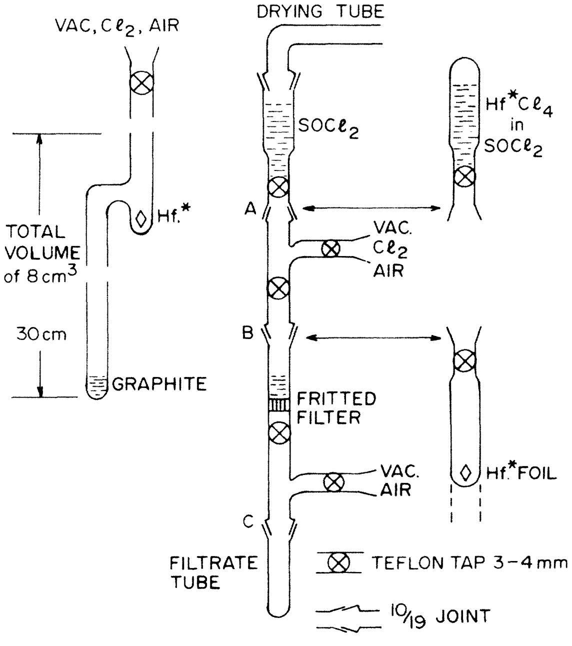

FIG. 1. Reactors for graphite with $HfCl_4 + Cl_2$ vapor on the left and with $HfCl_4$ dissolved in $SOCl_2$ on the right.

2. Preparation from $HfCl_4$ solution in $SOCl_2$

On the far right of Fig. 1, the Hf foil has been sealed into a 12-mm o.d. tube. This was attached to the upper system at *B* in place of the fritted filter shown in Fig. 1. It was evacuated to 1 μm before 200 mm of Cl_2 was admitted. Gentle heat produced $HfCl_4$. The excess Cl_2 was removed to a liquid-nitrogen trap at 1 μm and $SOCl_2$ liquid was admitted from the dispenser at the top of the system to give a saturated solution at 20 °C. The tap to the tube containing this solution was then closed so that the tube could be removed and used in place of the $SOCl_2$ dispenser at the top of the system. A weighed graphite sample was next placed on the fritted glass filter. This unit was attached at *B* and the system from *A* to *C* was evacuated to 1 μm. The tap below the filter was then closed and $HfCl_4$ solution was admitted to cover the graphite for a known time (usually overnight). The tap below the filter was then opened to allow the solution to flow into the filtrate tube. The system from *A* to *C* was again evacuated to 1 μm and the taps above and below the graphite were closed so that this section alone could be removed and placed in the spectrometer for the correlation measurements. It could obviously be returned to the dispensing system and, by appropriate evacuations and tap operations, washed with pure solvent or treated with more solution. The taps and joints were lightly lubricated with fluorinated grease. The weight increase of an 0.080 g sample of graphite was about 0.02 g. If this increase was all $HfCl_4$ then $C_{100}HfCl_4$ was the product. However, some of the 0.02 g was probably $SOCl_2$, but the exact amount could not be determined. More important was the fact that further washing with solvent and evacuation did not change the PAC spectrum.

B. TDPAC measurements

Using a detector system comprising four NaI(Tl) spectrometers,[9] the angular correlation of the 133—482-keV γ-γ cascade in the daughter nucleus ^{181}Ta was recorded to give information on the quadrupole interaction between the intermediate state and the local EFG. Using a ^{60}Co source with energy windows set to select the 133- and 482-keV γ rays in the Compton continuum, the time resolution (full width at half-maximum) was found to be 2.1 ns. By using the most sensitive scale (50 ns) on the time-to-amplitude converter when adjusting delays, the centroids of the prompt peaks could be positioned to within 40 ps, thus locating the zero time to within approximately one-tenth of a channel for the time scale (100 ns) used for the measurements. The four time spectra, corresponding to two sets of 90° and 180° angular correlations, were routed to quadrants of a multichannel analyzer and the perturbation factor determined directly from the data by

$$G_{22}(t)=\frac{2}{3A_2}\left[\left[\frac{W_{13}(\pi,t)W_{24}(\pi,t)}{W_{14}(\pi/2,t)W_{23}(\pi/2,t)}\right]^{1/2}-1\right],$$

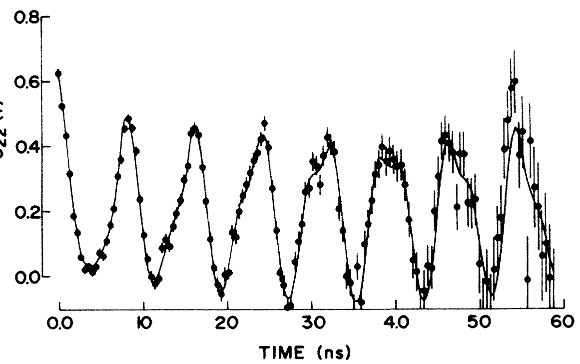

FIG. 2. The perturbation factor at room temperature for a sample of graphite-$HfCl_4$ prepared by the vapor-transport technique in the presence of chlorine. The solid line represents the theoretical fit based on Eq. (2).

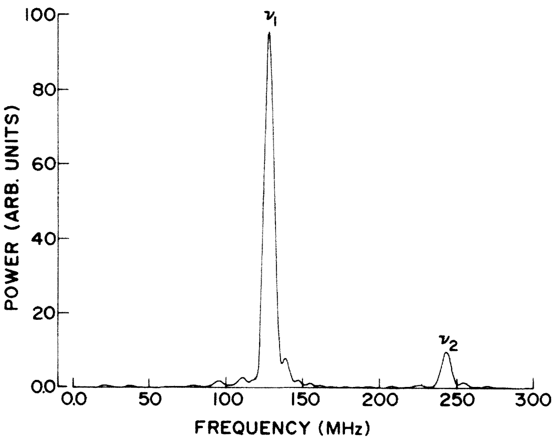

FIG. 3. The Fourier power spectrum of $G_{22}(t)$ in Fig. 1. The frequency ratio ν_2/ν_1 was used to determine ν_q and η in Table II [square brackets].

where $W_{ij}(\theta,t)$ refers to the angular correlation recorded by detectors i,j with A_2 corrected for finite solid-angle effects.

IV. RESULTS

Figure 2 shows the perturbation factor obtained at room temperature for a sample of graphite-$HfCl_4$ prepared from Madagascar flakes jet-milled to 2 μm across. The composition of this sample, determined by weighing, was $C_{21}HfCl_4$. The solid line is a theoretical fit of the form

$$G_{22}(t)=c_0G_s(t)+c_1\exp(-t/\tau)\ , \qquad (2)$$

where $c_0+c_1=1$ and $G_s(t)$ is a static interaction of the form in Eq. (1) corrected for finite-time resolution and for a finite width δ in the quadrupole interaction. In the event that the graphite flakes may not have been truly randomly oriented, the s_{2n} coefficients were treated as free parameters in performing the fits. A reasonable fit could only be achieved by incorporating also the time-dependent term with time constant τ. The parameters obtained from the fit are listed in Table I.

Figure 3, which indicates the Fourier power spectrum of the data in Fig. 2, allows direct determination of the quadrupole frequencies and from their ratios another method of determining the asymmetry parameter η.[7] By making an appropriate choice of the apodization function,[10] the true frequencies are concentrated in relatively narrow regions of the frequency spectrum while the noise is distributed over the entire bandwidth. From Table I it can be seen that consistent agreement is obtained for both methods of analysis.

Runs were also performed at liquid-nitrogen temperature on this sample in an attempt to elucidate the origin of the time-dependent component. These data are also indicated in Table I. An additional sample was prepared with the 2-μm flakes which had a composition of $C_{19}HfCl_4$. A preparation using larger Madagascar flakes (120–140 mesh) yielded $C_{80}HfCl_4$. Both of these samples generated

TABLE I. Quadrupole interaction parameters at room and liquid-nitrogen temperatures for graphite-$HfCl_4$ prepared by the vapor-transport method. The interactions are defined in Eq. (2). Where possible ν_q and η [square brackets] were also determined from the frequency ratios in the Fourier spectrum of Fig. 3.

Interaction	%	ν_q (MH$_z$)	η	δ	V_{zz} (10^{18}/cm^2)	τ (ns)
$G_s(t)$	78(2)	813(10)	0.21(2)	0.00(2)	1.20(8)	
↑		[818(10)]	[0.20(3)]			
293 K						
↓						
$\exp(-t/\tau)$	22(1)					0.9(1)
$G_s(t)$	52(2)	813(10)	0.22(2)	0.00(2)	1.02(8)	
↑						
77 K						
↓						
$\exp(-t/\tau)$	48(2)					0.4(1)

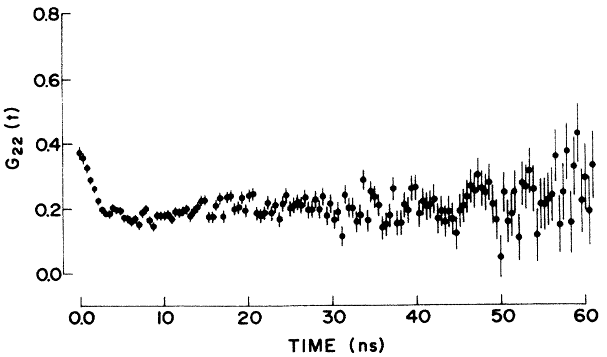

FIG. 4. The perturbation factor at room temperature for a Spheron 6 carbon black sample with adsorbed ^{181}HfCl$_4$.

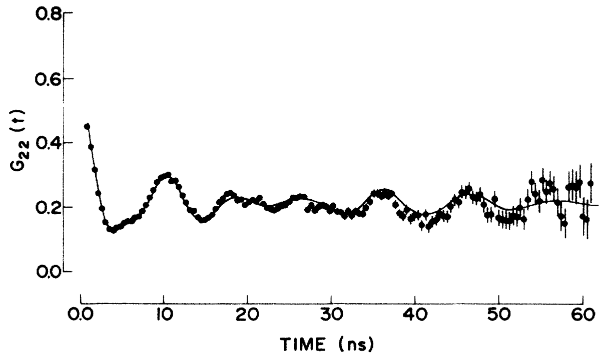

FIG. 6. The perturbation factor at room temperature for a sample of graphite-HfCl$_4$ prepared from solution in SOCl$_2$. In the early part of the spectrum the error bars are contained within the size of the data points. The solid line represents the theoretical fit based on Eq. (3).

time spectra at $T=293$ K which are indistinguishable from that of the C$_{24}$HfCl$_4$ sample.

In order to verify that the signal observed in Fig. 2 was in fact from intercalated HfCl$_4$, TDPAC measurements were also performed on a sample prepared using Spheron 6 2700 °C, a Cabot Carbon product with an area of 100 m^2 gm^{-1} which does not form an intercalation compound. Figure 4 shows that the data obtained from this sample with HfCl$_4$ adsorbed on carbon black is quite different in character, being heavily damped with no periodic signal apparent. Furthermore, measurements on free Hf metal and anhydrous HfCl$_4$ revealed distinctly different frequencies in the time spectra. Details on the latter will appear in a separate publication.

An attempt was made to intercalate HfCl$_4$ without the presence of chlorine in the reaction vessel. The results of this are shown in Fig. 5, which indicates clearly that no intercalation has taken place.

The results for HfCl$_4$ intercalated by using the solvent SOCl$_2$ are presented in Fig. 6 together with the theoretical fit. In this case the fit required two static interactions of the type (1), plus a time-dependent interaction, with

$$G_{22}(t)=c_1G_s^{(1)}(t)+c_2G_s^{(2)}(t)+c_3\exp(-t/\tau)\ . \qquad (3)$$

Figure 7 shows the corresponding Fourier power spectrum, while Table II contains a summary of the results for this sample.

V. DISCUSSION

In all cases of samples prepared by the vapor-transport technique and maintained at $T=293$ K, the data could be fitted according to Eq. (2) with a combination of a single static (78%) and time-dependent (22%) interaction. Regardless of the type or size of graphite flakes used, the fitted parameters for all measurements at the same temperature were virtually indistinguishable. This result is in contrast to that obtained for graphite-InCl$_3$.[11] Such a situation could result from incomplete intercalation of the graphite host, with the formation of islands of intercalated material in which the EFG is well reproduced.

The quadrupole frequency for the static component was determined to be $\nu_q=811\pm12$ MHz with essentially no in-

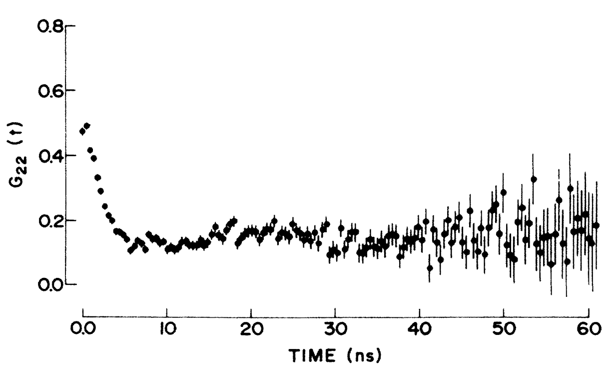

FIG. 5. The perturbation factor at room temperature for a sample prepared by the vapor-transport technique, but in the absence of chlorine. This should be compared with Fig. 2.

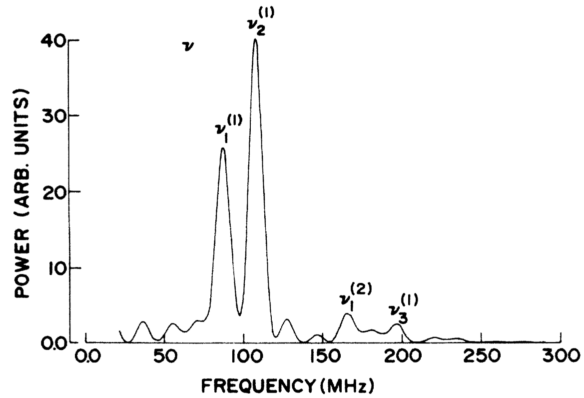

FIG. 7. The Fourier power spectrum of $G_{22}(t)$ in Fig. 6. The frequency ratios $\nu_2^{(1)}/\nu_1^{(1)}$ and $\nu_3^{(1)}/\nu_1^{(1)}$ were used to determine ν_q and η in Table II [square brackets]. Of the second interaction $G_s^{(2)}$ in Eq. (3) only $\nu_1^{(2)}$ was resolved.

TABLE II. Quadrupole interaction parameters at room temperature for graphite-$HfCl_4$ prepared from solution in $SOCl_2$. The interactions are defined in Eq. (3). Where possible ν_q and η [square brackets] were also determined from the frequency ratios in the Fourier spectrum of Fig. 7.

Interaction	%	ν_q (MH$_z$)	η	δ	V_{zz} (10^{18} V/cm^2)	τ (ns)
$G_s^{(1)}(t)$	19(1)	393(5) [393(5)]	0.74(5) [0.75(6)]	0.04(1)	0.58(3)	
$G_s^{(2)}(t)$	41(2)	1128(20)	0.04(3)	0.10(2)	1.67(10)	
$\exp(-t/\tau)$	40(2)					0.93(3)

homogeneous broadening ($\delta \approx 0$). Previous experimental work, as reviewed by Selig and Ebert,[2] suggests that metal halides are structurally undistorted upon intercalation from the vapor phase. Since the structure of $HfCl_4$ is not commensurate with that of graphite, if steric factors imposed by the graphite host lattice were important in determining the conformation of intercalated $HfCl_4$, one would expect to observe a distribution of quadrupole frequencies instead of a narrow line. In accordance with the general characteristics of graphite-metal halides, the static site most probably corresponds to the $+4$ oxidation state of the hafnium, since the $+3$ state can only be obtained under extraordinary conditions and in a nonstoichiometric mixed phase.

Since the decay lifetimes (~ 1 ns) associated with the time-dependent portion were comparable with the system resolving time, a detailed analysis was performed for the effects of finite resolving time over the first 4–5 ns of the time scale where the effects of this term are manifested. The results obtained using analytic expressions[12] were compared with those derived from a numerical convolution of the prompt resolution peak (approximated well by a Gaussian shape) with the uncorrected equation for $G_{22}(t)$. Agreement to the fifth significant figure was obtained, except at $t=0$ where the agreement was to the third significant figure.

The question arises as to whether c_1 represents a true time-dependent component, or whether, for example, it could result from a broad distribution of static sites with frequencies beyond the system resolution. Certainly the measurements at liquid-nitrogen temperature are consistent with the presence of a mobile species. The change in the time spectrum with temperature was detected for all the graphite-$HfCl_4$ samples studied. Moreover, if the temperature of a given sample was cycled between room and liquid-nitrogen points, the change was observed to be reversible and reproducible. A time-dependent component could correspond to a randomly fluctuating EFG caused possibly by diffusion or rapid rotation of the probe. From Table I the results at 77 K indicate an increase in the number of sites occupied by this species (from 21% to 48%) whereas its associated time constant becomes appreciably smaller ($\tau_1 = 0.4 \pm 0.1$ ns). At the lower temperature a decrease in charge transfer to $HfCl_4$ molecules would presumably result in a lower fraction of these in static sites.

The nature of such a time-dependent species is open to conjecture. It has been established that in the case of some metal chlorides, chlorine not only enhances the intercalation but is incorporated into the graphite with the intercalant.[2] If we ascribe the time-dependent species to the formation of a $HfCl_4$-chlorine complex, then using Frey's composition[13] at room temperature, we obtain

$$(1-c_1)HfCl_4 + c_1 HfCl_4 \cdot 2Cl_2 \rightarrow HfCl_{4.77}$$

giving $c_1 = 0.19$, in reasonable agreement with our fitted value of 0.22 ± 0.01 using Eq. (2).

The data for the samples intercalated by dissolving in $SOCl_2$ show a more complex and less well-defined perturbation signal. The EFG in this case is modified considerably by the presence of $SOCl_2$ or other complexes, resulting in two sites for static interactions plus a third time-dependent species. The c_1 component of Eq. (3) is well defined, accounting for 19% of the signal, with $\nu_q^{(1)} = 393 \pm 5$ MHz. On the other hand, the quadrupole frequency for the second static interaction with $c_2 = 0.41$ is high enough ($\nu_q^{(2)} = 1121 \pm 20$ MHz) that only the lowest frequency of the triplet is resolved in the Fourier power spectrum of Fig. 7.

Using the value $Q = 2.51(15)$ barns for the quadrupole moment of the intermediate state,[14] the EFG components were calculated as shown in Table II for each of the samples. A theoretical calculation of the EFG would be invaluable in elucidating structural details of these systems, but to our knowledge none is available to date.

The role of chlorine in the preparation of these metal chloride intercalation compounds is of great interest and such studies are currently in progress.

---

[1] E. Stumpp, Mater. Sci. Eng. 31, 53 (1977).

[2] H. Selig and L. B. Ebert, Adv. Inorg. Chem. Radiochem. 23, 281 (1980).

[3] R. C. Croft, Aust. J. Chem. 9, 184 (1956).

[4] E. Stumpp (private communication).

[5] S. R. Dong, S. El-Kateb, J. G. Hooley, and P. W. Martin, Solid State Commun. 45, 791 (1983). Note errata in this paper for the quoted EFG components owing to an incorrect value of

Q. Using $Q = 0.83(16)$ barns from Ref. 10, the values reported here should be multiplied by the constant factor 3.024.

[6] H. Frauenfelder and R. M. Steffen, in *Alpha-, Beta- and Gamma-Ray Spectroscopy,* edited by K. Siegbahn (North-Holland, Amsterdam, 1965), Vol. 2, p. 997.

[7] E. Gerdau, J. Wolf, H. Winkler, and J. Braunsforth, Proc. R. Soc. London Ser. A **311**, 197 (1969).

[8] W. V. Prestwich, I. A. Cunningham, and T. J. Kennett, Hyperfine Interact. **12**, 329 (1982).

[9] P. W. Martin, S. El-Kateb, and U. Kuhnlein, J. Chem. Phys **76**, 3819 (1982).

[10] F. J. Harris, Proc. IEEE **66**, 51 (1978).

[11] S. R. Dong, J. G. Hooley, and P. W. Martin, Carbon **22**, 453 (1984).

[12] R. Beraud, I. Berkes, J. Daniere, G. Marest, and R. Rougny, Nucl. Instrum. Methods **69**, 41 (1969).

[13] G. Frey, Diplomarbeit, Technische Universität Clausthal, 1975 (result quoted in Ref. 2).

[14] G. Netz and E. Bodenstedt, Nucl. Phys. **A208**, 503 (1973).