

## Islandlike in-plane structure and vibrational behavior of $\text{NiCl}_2$ intercalated in graphite

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Accurate extended x-ray-absorption fine-structure (EXAFS) measurements, at room temperature, have been made on nickel dichloride single crystals and on the same compound intercalated in graphite, in order to study the vibrational and structural properties of the latter low-dimensional system. EXAFS spectra have been performed both on the  $K$  edge of Ni and on the  $K$  edge of Cl. The  $\text{NiCl}_2$  molecules intercalated between the hexagonal planes of graphite form clusters or islands, about 10 Å apart on the same layer, with a Ni triangular lattice incommensurate with the graphite host lattice. However, in spite of the expected distortion of the intercalated compound, our results indicate that the  $\text{NiCl}_2$  molecule exhibits no deformation upon intercalation with respect to the pristine crystal. A theoretical simulation of the EXAFS spectra of the single crystal has confirmed the recent diffractive parameters reported in the literature.

### I. INTRODUCTION

Graphite intercalation compounds (GIC) have warranted considerable attention because of their interesting properties,<sup>1–5</sup> probed by many different experimental techniques.<sup>1</sup> We recall only a few of these characteristics, such as the low-dimensional behavior, due to the layered structure, the charge transfer from the intercalant to the graphite in donor compounds and vice versa in acceptor compounds,<sup>2</sup> or the low-dimensional magnetism. In  $\text{NiCl}_2$ -GIC it has been shown how the existence of islands can produce superferromagnetic effects<sup>3,4</sup> that depend on temperature. It is then important to understand how this enhanced effect correlates with the dimension of the clusters introduced along the planes of the graphite when, at high stage, it is expected that the  $\text{NiCl}_2$ -GIC will behave as an ideal “multilayered system.”

Pristine  $\text{NiCl}_2$  (Refs. 6 and 7) has a rhombohedral or hexagonal structure,<sup>8</sup> but, upon intercalation between the hexagonal planes of the graphite, it can be considered as having octahedral building blocks with a metal atom in the center, disposed with a triangular face lying on the graphite planes.

The intercalant molecular lattice is incommensurate<sup>3</sup> with the host hexagonal structure, and therefore distortion of the pristine short-range distances is expected, together with a strong modification of the vibrational behavior of the molecule stressed within the graphite lattice. This implies reduced ordering dependent not only on the stage  $n$  of the intercalation but also on the limited dimension of the intercalated clusters. Consequently, the

magnetic behavior, magnon modes, magnetic phase diagrams, magnetic-dipole interactions, and intralayer and interlayer coupling related to phonon dispersion are greatly modified.<sup>3,4</sup>

The structural and vibrational investigation of this graphite intercalation compound then appears very interesting: we used the extended x-ray-absorption fine-structure (EXAFS) spectroscopy<sup>9,10</sup> as a powerful technique in obtaining information about the previously mentioned properties. This method, in fact, allows the determination of the local structure around each atomic species: interatomic distances, coordination numbers, and the Debye-Waller factor can be obtained by this method with high accuracy. The method also allows us to check if the sample is pure enough, because the presence of contaminants would show a corresponding frequency in the spectrum with an amplitude related to the amount of the spurious elements, as shown in Refs. 11 and 12.

The argument of this paper is presented in the following sections. Experimental details are presented in Sec. II. In Sec. III we show the results obtained on  $\text{NiCl}_2$  single crystals by the same technique. These measurements have been done as a reference for the  $\text{NiCl}_2$ -GIC EXAFS spectra, presented in this same section, where the results are discussed and interpreted.

### II. EXPERIMENT

The EXAFS spectra have been performed on the  $K$  edge of the transition metal in the range 8250–9200 eV and on the  $K$  edge of the chlorine in the range 2790–3210

eV, both for the reference compound and for the NiCl<sub>2</sub>-GIC. All the measurements have been done at room temperature.

As the commercial sample of NiCl<sub>2</sub>, being hygroscopic, can present even a small percentage of contaminants, such as oxygen or water for long storage or improper handling, our sample was home prepared. Single crystals of NiCl<sub>2</sub> were obtained from the vapor phase by the dynamical transport method at temperatures around 700°C. Chlorine gas was passed through a quartz pipe where reaction occurred. The obtained samples consisting of large crystals have been stored in vacuum; some surface layers have always been peeled off immediately before the measurements that have been done in vacuum by means of the fluorescence technique.

The samples of the intercalated compounds, in powder form, were purchased from the Alfa Products, packed and handled under dry argon, and observed in the same configuration of the reference crystal under vacuum, after having been reduced to a thin layer. Although the stage of our GIC is not known, it is, however, quite high, since

the dilution of the chloride molecule into the graphite corresponds to about 20%.

The experiment has been done using the PULS x-ray beamline facility of Frascati National Laboratory. The radiation was monochromatized by a Si(111) channel cut crystal and the radiation was detected and recorded in the conventional way.<sup>9</sup> The average photon flux was 10<sup>9</sup> photons/s and the resolution was about 2 eV. The incident and the fluorescent x-ray beam intensity was measured by an ionization chamber and a NaI(Tl) detector, respectively. Several measurements have been collected on different samples to check for reproducibility.

### III. RESULTS AND DISCUSSION

The x-ray fluorescence spectra  $I_F$ , taken on the Ni *K* edge and on the Cl *K* edge, were analyzed with respect to the incoming flux  $I_0$  according to the standard procedure<sup>13</sup> used for EXAFS measurements. The EXAFS oscillations have been obtained by fitting the absorption coefficient above the edge with a polynomial curve, in the

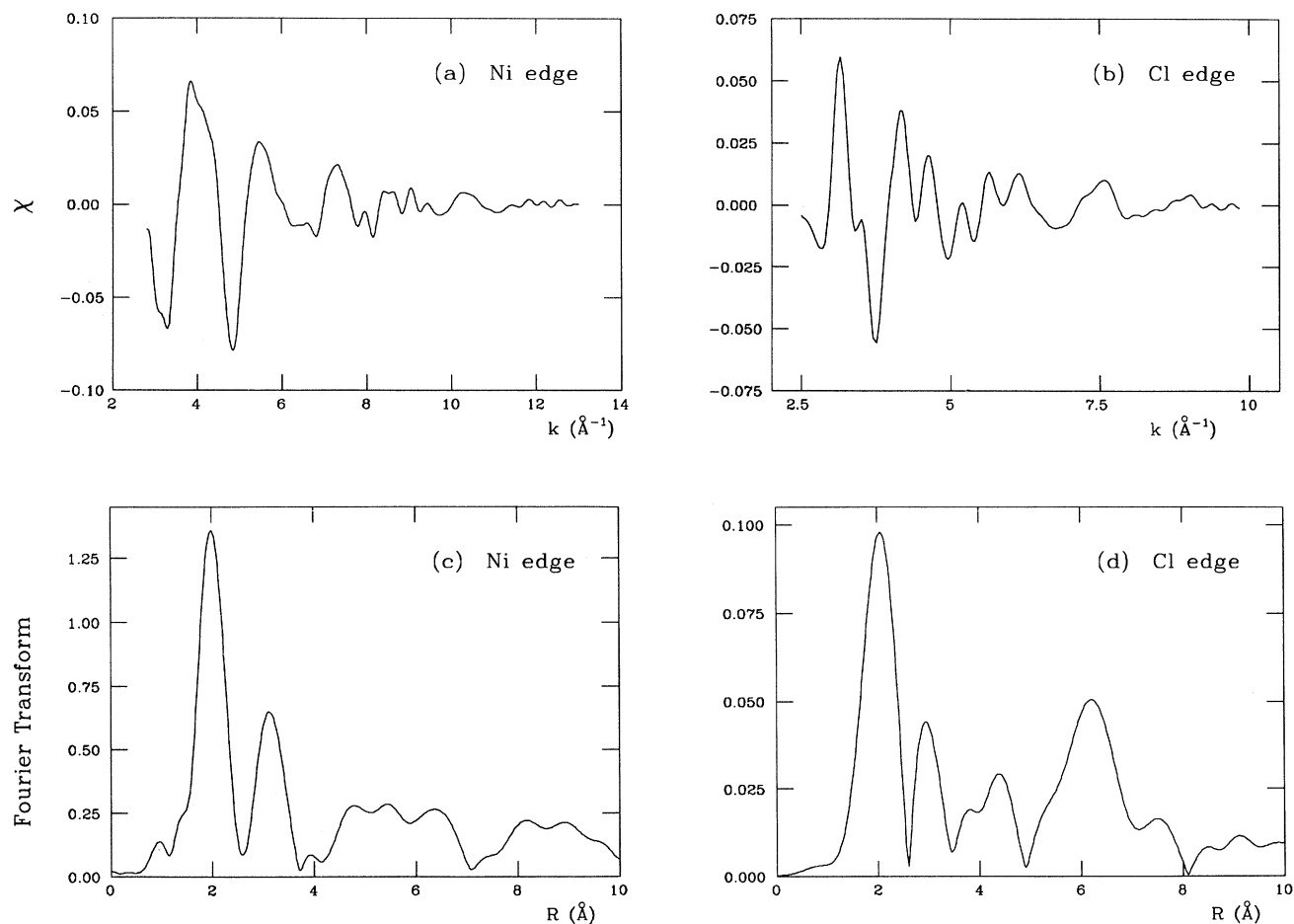


FIG. 1. In the upper part, for the NiCl<sub>2</sub> single crystal, the EXAFS spectra  $\chi(k)$  are shown, obtained on (a) the Ni *K* edge and (b) the Cl *K* edge. In the lower part, the corresponding magnitude of the Fourier transforms is shown.

$k$  range  $2\text{--}13 \text{ \AA}^{-1}$  for the Ni spectra and  $2.5\text{--}10 \text{ \AA}^{-1}$  for the Cl spectra.

### A. NiCl<sub>2</sub> single crystal

In Fig. 1 the EXAFS spectra obtained for the NiCl<sub>2</sub> single crystal are shown together with the usual Fourier transforms (FT), which give the absolute nearest-neighbor (NN) peaks in the real space if the phase shifts are known.<sup>14</sup> These can be obtained by the theoretical model of Teo and Lee,<sup>14</sup> taking into account the many-body effects that attenuate the EXAFS amplitude.<sup>10</sup>

According to Stern,<sup>10</sup> the EXAFS spectrum is represented, with the usual meaning of the symbols, by the following expression:

$$\chi(k) = \sum_i \frac{N_i S_0^2(k) F_i(k)}{k r_i^2} P_i(k) e^{-2(r_i - \Delta)/\lambda} \times \sin[2k r_i + \phi_i(k)],$$

which takes into account the previously mentioned many-body effects due to two main effects. The first is caused by the relaxation of the final state with a corresponding decrease in the many-electron dipole matrix element. The overlap between initial- and final-state electrons gives an attenuation  $S_0^2$  (Ref. 15) between 0.6 and 0.9 in the EXAFS amplitude dependent on the center atom. The second is due to inelastic energy losses already included in the EXAFS expression by means of a mean free path  $\lambda$ , which, however, should be corrected with a suitable parameter  $\Delta$  modifying the exponential attenuation caused by the lifetime effects.

In Ref. 10 these effects have been checked for MnCl<sub>2</sub>, FeCl<sub>2</sub>, and CoCl<sub>2</sub>, of the same class of our samples. We observe at this point that a comparison has been made with the analogous spectra obtained from the published data of Stern for CoCl<sub>2</sub> and MnCl<sub>2</sub>, which have been transformed in the same range as ours. In Fig. 2 the logarithm of the amplitude ratios of CoCl<sub>2</sub> and MnCl<sub>2</sub> is shown, obtained from Ref. 10, to NiCl<sub>2</sub>, versus  $k^2$ . In both cases the ratio is nearly linear with intercepts near zero; this indicates that the EXAFS amplitudes are the same except for differences in  $\sigma^2$ . Thus, the comparison shows the similarity of our data with those of Ref. 10, so that we are allowed to use the values reported by Stern for the amplitude attenuation  $S_0^2=0.7$  and the core radius  $\Delta$ , which for this class of materials is of the order of the first coordination shell  $\Delta \approx r_i$ .

The asymptotic value at  $k=0$  in Fig. 2 actually demonstrates that we have a further amplitude attenua-

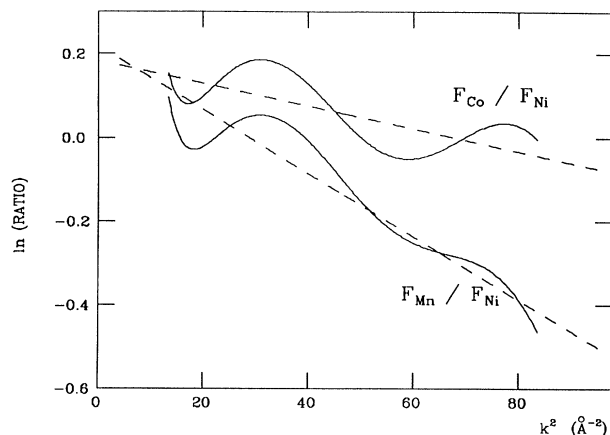


FIG. 2. Logarithm of the experimental amplitude ratios of CoCl<sub>2</sub> ( $A_{Co}$ ) to NiCl<sub>2</sub> ( $A_{Ni}$ ) and of MnCl<sub>2</sub> ( $A_{Mn}$ ) to NiCl<sub>2</sub>. The dashed straight lines are the fits indicating the changes to the Debye-Waller factor for these compounds.

tion of the order of 20%: this effect should be ascribed to our detection method because, as is well known, the fluorescence yield for thick samples is reduced according to the formulas of Ref. 16. This amplitude reduction has been taken into account in evaluating our experimental results, as reported in the next section.

Before discussing our results, it is worth recalling the structure of NiCl<sub>2</sub>. It can be thought of<sup>9</sup> as a rhombohedral or a hexagonal structure. Its unit cell is a rhombohedron ( $a_0=6.13 \text{ \AA}$ ;  $\alpha=33^\circ 36'$ ) with Ni at (0,0,0) and Cl at  $(u, u, u)$ ,  $(\bar{u}, \bar{u}, \bar{u})$ , or equivalently in the hexagonal system the Ni atoms can be arranged at the corners and at the center of hexagons in layers shifted relative to one another by  $(0, \pm a/\sqrt{3}, \pm c/\sqrt{3})$  ( $a=3.543 \text{ \AA}$ ;  $c=17.335 \text{ \AA}$ ); the  $z$  coordinate of a chlorine is shifted by  $\pm uc$  with respect to a Ni atom ( $u \approx 0.255$ ).

The previous data, however, have been checked and refined in 1963 by Ferrari *et al.* (Ref. 17), who give for a single crystal  $a=3.483 \pm 0.006 \text{ \AA}$ ;  $c=17.40 \pm 0.03 \text{ \AA}$ . The distance  $d_{Ni-Cl}=2.426 \pm 0.008 \text{ \AA}$ ,  $d_{Ni-Ni}=a$ , while for  $d_{Cl-Cl}$  three values are possible:  $3.385 \pm 0.016$ ,  $3.483 \pm 0.006$ , and  $3.674 \pm 0.016 \text{ \AA}$ . The coordination for Ni-Cl is 6; for Ni-Ni, 6; for Cl-Cl, 8. In the literature, however, values are used between those reported above.<sup>18,19</sup>

TABLE I. For both samples NiCl<sub>2</sub> single crystal and NiCl<sub>2</sub>-GIC the first- and second-shell position is reported as deduced directly from the Fourier transforms of Figs. 1 and 3, and after inclusion of the phase shift  $\phi$  obtained from a theoretical simulation (see text).

Samples	First coordination shell: Ni-Cl			Second coordination shell: Ni-Ni		
	$R_{FT} (\text{\AA})$	$\Phi (\text{\AA})$	$R (\text{\AA})$	$R_{FT} (\text{\AA})$	$\Phi (\text{\AA})$	$R (\text{\AA})$
Crystal	$1.98 \pm 0.02$	0.47	$2.45 \pm 0.02$	$3.11 \pm 0.02$	0.37	$3.48 \pm 0.02$
GIC	$1.94 \pm 0.02$	0.47	$2.41 \pm 0.02$	$3.12 \pm 0.02$	0.37	$3.49 \pm 0.02$

As is well known, the Fourier transforms of the EXAFS data give the shell position if the phase shift for the couple scatterer absorber is known. This can be obtained either by a reference model compound or by means of a theoretical simulation. We have used the theoretical method of Teo and Lee, who have tabulated the amplitudes and the phase shifts accurately, to get the calculated curves for many compounds.

First- and second-neighbor coordination numbers and the Debye-Waller factors  $\sigma^2$  were obtained from the usual plot of  $\ln[A_s(k)/A_m(k)]$  versus  $k^2$ ,<sup>8</sup>  $A_s(k)$  and  $A_m(k)$  being the amplitudes of the inverse FT of the sample and of the reference model compound, respectively.

This allows us to compare theory and experiment for both the first and the second coordination shell. In Table I we compare our results with the known values. As can be seen, the agreement with the diffractional data is excellent within the experimental accuracy.

### B. NiCl<sub>2</sub>-GIC

For the samples NiCl<sub>2</sub>-GIC, the spectra  $\chi(k)$  and the corresponding FT are shown in Fig. 3. Data have been

TABLE II. Measurements on the Cl *K* edge: first- and second-shell position as deduced without any phase-shift correction for both samples, from the FT of Figs. 1 and 3.

	First coordination shell: Cl-Ni	Second coordination shell: Cl-Cl
Samples	$R_{FT}$ (Å)	$R_{FT}$ (Å)
Crystal	$2.03 \pm 0.02$	$2.95 \pm 0.02$
GIC	$2.00 \pm 0.02$	$2.98 \pm 0.02$

collected and reported both for the Ni *K* edge and the Cl *K* edge. For the intercalated samples, comparison with the spectra of the single crystal has allowed the evaluation of the expected structure distortion and of the relative Debye-Waller factor. We obtained a value  $\Delta r = 0.04 \pm 0.03$  Å, which shows that, in spite of expectation, the chloride molecule intercalates without significant short-range distortion, its structural configuration being unchanged with respect to the parent material.

This is confirmed by the evaluation of the first-shell coordination number, obtained by the standard analysis

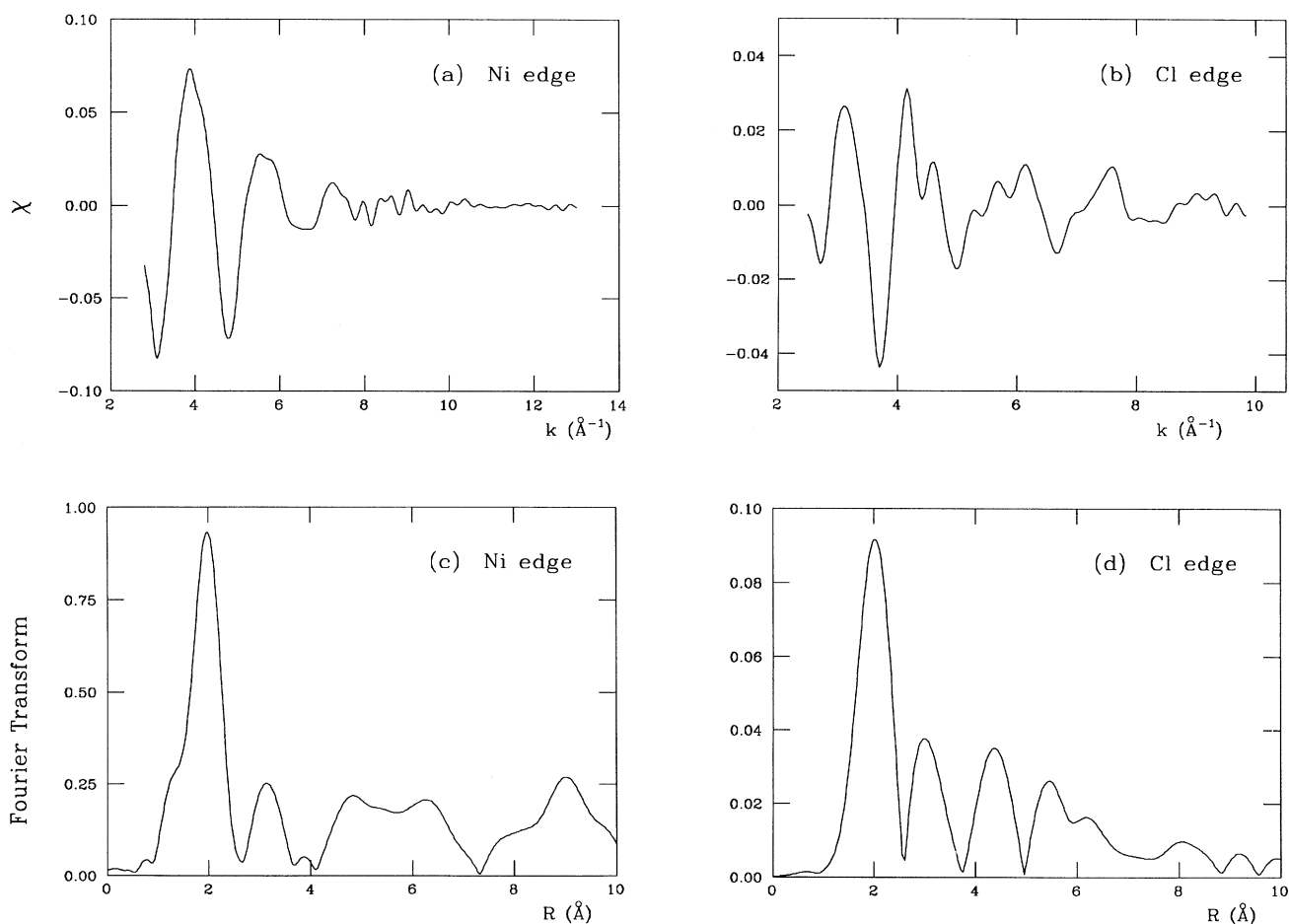


FIG. 3. Same as Fig. 1 for NiCl<sub>2</sub>-GIC.

TABLE III. Comparison of the coordination number  $N$  of the intercalated compound with respect to the same quantity  $N_0$  of the crystal. The variation of the Debye-Waller factor is also reported. The values are obtained from the measurements on the  $K$  edge of Ni for the first and second shell.

Samples	First coordination shell: Ni-Cl		Second coordination shell: Ni-Ni	
	$N/N_0$	$\Delta\sigma^2$ ( $\text{\AA}^2$ )	$N/N_0$	$\Delta\sigma^2$ ( $\text{\AA}^2$ )
Crystal	1	0	1	0
GIC	$1.05 \pm 0.05$	$0.0046 \pm 0.0005$	$0.45 \pm 0.05$	$0.0007 \pm 0.0005$

as being equal to unity. However, the analysis of the second shell, Ni-Ni, confirms that the  $\text{NiCl}_2$ -GIC intercalates in small clusters or islands since the coordination Ni-Ni reduces to about half of the crystalline value. This implies clusters of 4–6  $\text{NiCl}_2$  molecules, as will be discussed in the following.

We observe at this point that the amplitude reduction due to the fluorescence detection does not affect (Ref. 16) the near-neighbor distances, while corrections are necessary to compensate for this amplitude reduction for a correct determination of coordination numbers and of Debye-Waller factors. Following Tan *et al.*,<sup>16</sup> we have evaluated these corrections for the pure and intercalated  $\text{NiCl}_2$ , which have been found to be the same within 10%, and therefore have a negligible influence on the coordination number and on the Debye-Waller factor of the intercalated compound relative to the crystalline one.

In Table II the peak positions of the first and the second shell are reported, obtained from the FT shown in Figs. 1(d) and 3(d).

Because these spectra are obtained by observing the  $K$  edge of chlorine, which is a light absorber, we have not found in the literature the corresponding phase shift. However, the comparison between the crystal and the intercalated compound shows, as before, no significant distortion of the molecule. In any case, the small contraction of the distance  $d_{\text{Cl-Ni}}$ , even though it is within the experimental uncertainty, is coherent with the one shown in Table I.

In conclusion, from the previous results we have deduced important information about the structural behavior of the intercalated molecule in comparison to the crystalline structure. First of all we want to emphasize that the EXAFS measurements have allowed us to check and discriminate between the diffraction data available in the literature for the crystal.

Further, the direct comparison between EXAFS spectra performed under the same experimental conditions

gives striking proof that the intercalation process does not produce, *per se*, a distortion of the host molecule even if the two lattices are incommensurate. We have also shown that the process of intercalation involves only a few molecules, as is clearly indicated by the coordination numbers. As a matter of fact, the first-shell coordination number of the metal (see Table III) is the same for the crystal as for the GIC, while the second-shell Ni-Ni relative coordination reduces to 0.45. This confirms that the  $\text{NiCl}_2$  is always present as a whole but without any long-range periodicity.

The previous conclusions are confirmed by the vibrational behavior of the intercalation compound referred to the crystal. The relative Debye-Waller factor  $\Delta\sigma^2 = \sigma_{\text{GIC}}^2 - \sigma_{\text{crystal}}^2$  (Table III) shows the increase of the absolute mean-square fluctuations in the interatomic distances of the GIC with respect to the crystal. This shows how the lack of three-dimensional periodicity can soften the lattice of the intercalation compound: this effect is of course stronger for the first-shell Ni-Cl than for the second one, Ni-Ni, because of the larger Ni-Ni distance and of the strong forces on the metal due to the chlorine first neighbors.

An alternate explanation is that the incommensurate graphite lattice is inducing a structural distortion of the Cl positions such that the disorder is increased, but the average position is unchanged. This model would also explain the smaller disorder increase of the Ni—Ni bond. For the purpose of discriminating between these effects, work is in progress to measure the temperature dependence of the disorder.

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