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Short Communication

EXAFS study of graphite intercalation compounds with transition metals (Fe, Ni)


Institute of Physics, Rostov State University, 344006 Rostov-on-Don, U.S.S.R.
Institute of Organo-Element Compounds, Academy of Sciences of the USSR, V-334 Moscow, U.S.S.R.

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Résumé. — Les composés d'insertion du graphite avec le Fe et Ni ont été étudiés par EXAFS. On montre que les atomes de fer forment des complexes de type π où le réseau de carbone joue le rôle d'un ligand aromatique polydentat. Par contre, les atomes de nickel forment des monocouches bidimensionnelles dans un arrangement hexagonal compact.

Abstract. — Graphite intercalation compounds with Fe and Ni have been investigated by means of EXAFS spectroscopy. Iron atoms have been shown to form π-type complexes where the carbon net acts as a polydentate aromatic ligand. In contrast, nickel atoms form two-dimensional monolayers with close-packed hexagonal structure.

Graphite intercalation compounds (GIC) offer opportunities for studying the intercalant species in quite unusual surroundings [1]. The case of the GIC with a transition metal (TM) is of great interest in view of their physical and chemical properties. Yet the local environment of the TM atoms and the nature of chemical bonds in the TM—GIC have been unknown until now. The EXAFS spectroscopy is at present quite commonly employed when studying the local environment of a specific atomic species in poorly ordered systems. EXAFS spectra of the Fe(Ni) K-edge in Fe(Ni)—GIC have been obtained at room temperature on an in-lab EXAFS spectrometer with the varied curvature bent crystal [2]. The TM—GIC studied were prepared by reduction of the stage 1 FeCl3—GIC (Samples 1, 2 and 3) and stage 2 NiCl2—GIC (Sample 4) with Li-diphenylide. All samples were obtained from powder graphite. The distances between the two graphene layers separated by a TM layer, found by an X-ray diffraction experiment, are 5.0—5.9 Å for Fe-GIC and 5.7—5.95 Å for Ni—GIC [3].

First let us consider the Fe—GIC. Some results concerning their Mössbauer spectra are given in [3]. They show that the Fe—GIC are not monophase systems. These spectra contain a doublet with such parameters as to warrant the conclusion that some iron atoms form weak complexes, possibly with graphene layers. Apart from the doublet, there is a hyperfine structure in the spectra indicating the presence of a magnetic phase of iron. Having examined the behavior of the hyperfine structure, the authors of reference [3] suggested that this phase in Fe—GIC was an ensemble of microclusters characterized by a considerable spread in their sizes and in the magnitude of the magnetic moment.

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Hereafter, the two phases, in which the iron atoms are present in the samples, will be referred to as the “complex” and the “magnetic” phase. The fraction of the iron atoms constituting the “magnetic” phase has been estimated by Mössbauer spectroscopy to be 5% in sample 1, 20% in sample 2 and 46% in sample 3.

Figure 1 shows the Fourier transforms (FT) of the EXAFS above the Fe K edge in the Fe—GIC as well as in ferrocene and the bulk iron. The last two are used as the model compounds for the “complex” and the “magnetic” phase, respectively. A preliminary analysis of FT of the Fe GIC spectra reveals that for the samples 1 and 2 containing mainly the “complex” phase (Figs. 1b, c) the predominant feature are the maxima whose positions and forms are close to those characterizing the maximum in the FT of the ferrocene spectrum (Fig. 1a) while their amplitudes are different.

![Fig. 1. The Fourier transforms of ferrocene (a), sample 1 of Fe—GIC with 5% of “magnetic” phase (b), sample 2 of Fe—GIC with 20% of “magnetic” phase (c), sample 3 of Fe—GIC with 46% of “magnetic” phase (d), bulk iron (e).](image-url)
In the following we shall discuss these spectra in greater detail, but now we consider the spectrum of sample 3 (Fig. 1d). The main peak distance in the FT of this sample exceeds the distance of the dominant peaks in samples 1 and 2 by 0.3 Å. The corresponding separation is thus too long for the Fe—C bond length. The contribution by the predominant maximum to the normalized EXAFS has been singled out using the Fourier filtering procedure. The form of the envelope of this contribution indicates that the corresponding shell of the neighbors is formed mainly by iron atoms. The position of the FT maximum corresponds to the Fe—Fe bond length of 2.22 Å, which is 10% less than the Fe—Fe distance in the bulk α-Fe. Furthermore, in the FT of the spectrum of sample 3 there is no intensive maximum in the 4.45 Å region that would correspond to the fourth shell in the BCC structure of α-Fe (Fig. 1e). The diminution of the interatomic distance, as compared to the bulk sample, and the relative reduction of coordination numbers for distant shells are typical of ultradispersion clusters of metals [4]. These results confirm the hypothesis claimed in reference [3] that the “magnetic” phase of iron in the samples of Fe—GIC is an ensemble of ultradispersion clusters located in pores and cracks of powder graphite.

Making use of harmonic approximation for atomic vibrations, one may write the normalized EXAFS in the usual form

\[ \chi = - \sum_j \frac{w_j N_j |f_j(\pi, \kappa)|}{\kappa R_j^2} \sin(2\kappa R_j + \psi_j) e^{-2R_j/\lambda} e^{-2\sigma^2 \kappa^2} \]

All notation in this formula corresponds to that used in reference [5]. We performed a single-shell and a two-shell fitting in order to determine the parameters corresponding to the main maximum in the FT of sample 3. It was assumed that this maximum was due either to Fe atoms only or to Fe and C atoms. In either case we failed to obtain realistic Fe—Fe distances. This points, most probably, to an important role of nongaussian effects due to a spread in the Fe—Fe distances arising from different sizes of the “magnetic” phase clusters.

Let us now return to samples 1 and 2. The nearest shell parameters for sample 1 were obtained by means of nonlinear fitting, with the values of \( N, R, \sigma \) and \( E_0 \) being varied. The amplitude and the phase functions for the Fe-C pair, used in the fitting, were determined from the EXAFS spectrum of ferrocene. The EXAFS from the nearest shell is isolated with the aid of the window function shown in figure 1b. The coordination number so obtained is 6.0, the Fe—C bond length is 2.01 Å while the value of \( \sigma^2 \) exceeds that in ferrocene by a mere 0.0007 Å². Since in sample 1 practically all iron atoms are in the “complex” phase, one may conclude that these atoms are localized in sites opposite the centers of carbon hexagons in the interlayer space of graphite, and the distance between the iron atoms and the nearest graphene layer equals 1.41 Å. This conclusion has been confirmed by the presence in the FT of the maxima \( C_2 \) and \( C_3 \) which correspond to distances to the second- and the third-nearest neighbors from the proximate graphene net (Figs. 1b and 2). The coordination of the iron atom and the bond length in the Fe GIC, found in the present work, are characteristic of stable sandwich π-complexes of iron. Hence, the iron atoms do indeed form the π-type complexes in which the nearest graphene layer serves as a polydentate aromatic ligand.

Next, making use of the results obtained for sample 3, we may attempt to estimate the amplitude of the maximum of the FT in sample 1 which, possibly, may appear due to 5% admixture of the “magnetic” phase of iron. Since, according to Mössbauer spectroscopy, the amount of the “magnetic” phase in sample 1 is ten times less than in sample 3, the amplitude of the corresponding
maximum must total a mere 0.03 Å⁻¹, which does not exceed the noise level. From an analysis of the dependence of the amplitude of FT maxima at \( r = 2.07 \) Å and \( r = 2.51 \) Å on the integration range one may infer that they are due to the presence of the neighboring atoms of iron. The maximum \( \text{Fe}_1 \) corresponds to the Fe–Fe bond length of 2.43 Å and the coordination number of approximately unity. The maximum \( \text{Fe}_2 \) corresponds to the bond length of 2.87 Å with its coordination number not easily amenable to determination in view of the proximity of the peak \( \text{C}_2 \). We have shown that not an admixture of the “magnetic” phase is responsible for these structural elements. Hence, the iron atoms localized in the interlayer space of graphite in the “complex” phase are not isolated but rather united in 2–4 atom clusters. Structural elements of these clusters are the dimers formed by the iron atoms coordinated to two neighboring carbon hexagons. One may see that the distance between their centers (2.46 Å) is close to the Fe–Fe₁ separation (Fig. 2). The maximum \( \text{Fe}_2 \) (Fig. 1b) can be associated with the distance between the nearest iron atoms which are coordinated to two neighboring carbon hexagons.

Turning to the FT of sample 2 (Fig. 1c), it is to be noted that the single-shell fitting of the first maximum indicates that the corresponding shell is constituted by carbon atoms with the coordination number equalling 4.7 and the Fe–C separation being 2.0 Å. This correlates well with the data of Mössbauer spectroscopy from which it follows that 80% of the iron atoms are in the “complex” phase in this sample. A shoulder on the main maximum located on the side ultra reflects superposition of contributions by the first shell of the “magnetic” phase of iron and by the Fe–Fe dimers from the “complex” phase. The FT structure in the range of distances greater than 2.25 Å resembles the FT structure of the spectrum of samples 1, differing from it only in a smaller amplitude.

Thus, the present investigation has confirmed the presence of two phases formed in the Fe–GIC by iron atoms and has made it possible to determine the structure of the “complex” phase.

Next we consider properties of the Ni–GIC. Figure 3 depicts the FT of the Ni–GIC and metallic nickel. The FT of the Ni–GIC contrasts sharply with the FT of the Fe–GIC, but is similar to the FT of the bulk nickel. The most pronounced maxima in the FT of the Ni–GIC correspond to three groups of the neighboring Ni atoms with the interatomic distances being 2.47 Å, 4.35 Å and 5.08 Å, respectively (Fig. 3a). The character of the imaginary part of the FT in the region of the maximum corresponding to the bond length of 5.08 Å is analogous to the behavior of the imaginary part of the FT of metallic Ni for the fourth “shadow” coordination shell, which points to the presence of focusing effect in the Ni–GIC. The FT maximum at \( r = 1.45 \) Å may
Fig. 3.— The Fourier transforms of Ni-GIC (a), bulk nickel (b), differential EXAFS (c) (see text). An absolute value—solid line, an imaginary part—dashed line.
be an artifact, but it may as well correspond to a real Ni—C bond length. In order to elucidate both the nature of this maximum and the origin of the shoulder on the main peak at \( r = 2.74 \text{ Å} \), we performed the following manipulation. Using the inverse Fourier transform technique, we singled out the amplitude and the phase functions for photoelectron scattering from the spectrum of metallic nickel. Then we subtracted from the Ni—GIC spectrum the contributions formed by shells of the Ni atoms with interatomic distances of 2.47 Å and 4.35 Å. Coordination numbers and Debye-Waller factors were chosen in such a way as to minimize the amplitude of the FT difference in the region of the coordination shells mentioned above. The obtained values of the coordination numbers are 5.2 and 6.1. The Debye-Waller factor \( \sigma^2 \) for the shell with the coordination number 5.2 coincided with that for the nearest coordination shell in the bulk Ni, while for the shell with the coordination number 6.1 it exceeded this value by 0.015 Å\(^2\). After this subtraction, the maxima with the coordinates less than 1.5 Å disappeared (Fig. 3c), which implies that they are side lobes. After the subtraction the shoulder at \( r = 2.74 \text{ Å} \) turned into a distinct maximum. Its imaginary part behaves similarly to that of the maximum with \( r = 3.32 \text{ Å} \), which is retained following the subtraction. These maxima correspond to the shells formed by carbon atoms. Values of the coordination numbers for carbon shells and the “shadow” shell of nickel may be obtained through a comparison of amplitudes of the corresponding contributions to the differential EXAFS with the backscattering amplitude of the carbon atom and with the envelope of the inverse FT of the “shadow” shell in metallic Ni. The coordination numbers obtained are 6 and 12 for the maxima corresponding to the Ni—C bond lengths of \( \sim 3.1 \text{ Å} \) and \( \sim 3.8 \text{ Å} \), respectively, and 4 for the “shadow” Ni atoms.

The set obtained of distances and coordination numbers for the Ni—Ni bonds, with the focusing effect taken into account, warrants the conclusion that the Ni atoms form islands of monolayer with a CPH structure and the interatomic distance of 2.47 Å. We estimated the size of these islands, located in the interlayer space of graphite, as follows. As has been shown in references [6, 7], nickel chloride intercalates graphite in the form of islands with the average diameter of 150 Å. The Ni atoms in this compound form a two-dimensional CPH structure with the Ni—Ni distance equal to 3.478 Å. The NiCl\(_2\) island transforms into an island of a two-dimensional Ni layer, and the interatomic distance Ni—Ni is reduced, as has already been proven, to 2.47 Å. Hence, a conclusion may be drawn that the diameter of the Ni islands would be of the order of 100 Å. This may account for the fact that the value of the coordination number for the third shell in the Ni—GIC is 4 rather than 6 as in the case of an infinite lattice with CPH structure.

The interatomic Ni—Ni distance in two-dimensional Ni layers in the Ni—GIC, found in the present work, is very close to the graphite lattice period. The presence in the FT of the Ni—GIC of maxima corresponding to the Ni—C bonds indicates that the positions of the monolayer and of the carbon lattice are correlated. In order to explain all details of the radial distribution function, the following model of Ni-GIC may be suggested. The structure of the Ni—GIC has the form ANiBANiBA. The islands of the Ni monolayer are located not in the middle of the interlayer space, but are slightly displaced towards one or the other of the graphene layers. Positions of the Ni atoms lie over the centers of carbon hexagons of the nearest net and under the sites of another net \( C_1 \) in such a manner that the Ni—C\(_1\) and Ni—C\(_1'\) bond lengths coincide and equal 3.1 Å (see Fig. 4). Simple geometrical relationship indicate that the distance between the Ni layer and the nearest net equals 2.8 Å. Thus, the total thickness of the filled layer being the sum of the last-named distance and the 3.1 Å separation from the more distant net comes out at 5.9 Å, which agrees with diffraction measurement date [3]. The maximum with \( r = 2.74 \text{ Å} \) in the FT of the differential EXAFS corresponds to a contribution arising from six \( C_1 \) atoms belonging to the nearest net as well as from one \( C_1' \) and three \( C_2' \) atoms of the more distant net. The maximum of the FT at \( r = 3.32 \text{ Å} \) can be associated with the contribution by six \( C_2 \) atoms from the nearest net and six \( C_3' \) atoms from the more distant net which all are equidistant from the Ni atom.
In order to answer the question as to the character of chemical bonding between the islands of the two-dimensional layer of Ni atoms and the graphite matrix, let us examine the Ni-C distance. The value of 3.1 Å, found in the present work, considerably exceeds the length of the covalent Ni-C bond, which amounts to 1.9—2.0 Å. At the same time, it is close to the sum of the covalent radius of Ni (1.25 Å) and the van der Waals radius of carbon (1.8 Å). Hence one may conclude that in a Ni—GIC the interaction between metal and graphite will be of a character intermediate between the covalent and the van der Waals interactions.

Thus, the atoms of transition metals form various types of chemical bonding with the carbon atoms in GIC, which gives rise to diversification of the observed physical and chemical properties of the TM GIC. The graphite intercalation compounds incorporating some other atoms of the 3d elements will be dealt with elsewhere.

References