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In situ x-ray study of an acceptor-donor heterostructure: Stage-1 $CoCl_2$-K-graphite intercalation compound

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The sequential intercalation process of potassium atoms into a stage-2 $CoCl_2$-graphite intercalation compound has been studied by *in situ* x-ray $(00l)$ scans. The heterostructure was made in a two-zone furnace with pre-prepared stage-2 $CoCl_2$-graphite intercalation compound and potassium metal sealed into an evacuated Pyrex glass tube. At temperatures $T_K = 130\,^\circ C$ and $T_s = 230\,^\circ C$ for the potassium metal and stage-2 $CoCl_2$-graphite intercalation compound, respectively, we observed a heterostructure with an interplanar spacing $d_H = d_1 + d_2 = 14.65$ Å, where $d_1 = 9.30$ Å corresponds to a C-$CoCl_2$-C stacking, and $d_2 = 5.35$ Å to a C-K-C stacking. This is the first observation of a donor-acceptor heterostructure. The kinetics of the transformation from stage-2 CoCl-graphite intercalation compound to stage-1 heterostructure can be understood by the movement of potassium atoms through Daumas-Hérold domains.

I. INTRODUCTION

The synthesis of stage-1 ternary heterostructure graphite intercalation compounds (GIC's) with the c-axis stacking C-A-C-B-C-A-C-B-C- $\cdots$ (C is a graphite layer; A and B are intercalant layers) has attracted considerable attention in recent years. This system provides an opportunity to understand the mechanism of intercalation. Its synthesis illustrates a unique way to get a novel GIC with a combination of two different kinds of intercalants such as alkali metals (donor type) and transition-metal chlorides (acceptor type). The stage-1 heterostructure GIC's reported so far are either the donor-donor type, such as, C-K-C-Cs-C (Ref. 1) or the acceptor-acceptor type, such as, C-$CoCl_2$-C-$FeCl_3$-C,[2] C-$BiCl_3$-C-$ReCl_{4.5}$-C,[3] or C-$TlCl_3$-C-$TlBr_3$-C.[4]

We report in this paper the first successful preparation of donor-acceptor-type stage-1 GIC which can be represented by the repeat sequence C-$CoCl_2$-C-K-C. This compound can be synthesized by sequential intercalation of potassium atoms into the stage-2 $CoCl_2$ GIC. The in-plane carbon—carbon bond length of the stage-2 $CoCl_2$ GIC is expected to be smaller compared to that of the pristine graphite, since the acceptor-type GIC's are known to exhibit a roughly linear decrease of the C—C bond length with charge transfer.[5] Thus, the sequential intercalation of potassium atoms into the stage-2 $CoCl_2$ GIC is considered to be equivalent to the interaction into pristine graphite under high pressure applied along the a axis. The growth kinetics are also studied by *in situ* x-ray $(00l)$ scans and discussed in terms of the Daumas-Hérold model.[6]

The stage-1 heterostructure MCl_2-K GIC's (M=Co, Mn, Ni) are also very attractive materials partly because they may provide a novel two-dimensional (2D) magnetic system of π and d electrons. In these compounds, electrons are transferred from the potassium atoms to the π band of graphite. The weak interaction between the increased number of π electrons and the localized $M_2{}^+$ spins may play a crucial role for establishing the 2D magnetic ordering, in a way similar to the donor type C_6Eu (Ref. 7) with Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction between the π electrons and the localized Eu spins.

II. EXPERIMENTAL

The stage-1 heterostructure $CoCl_2$-K GIC sample was prepared from a single crystal of Kish graphite (SCKG) by a sequential intercalation procedure. A stage-2 $CoCl_2$ GIC was first prepared from SCKG in the usual manner.[8] This sample was transferred under He atmosphere into a Pyrex tube containing pure potassium metal. After evacuating, the glass tube was sealed off and placed into a two stage vertical x-ray furnace, with the potassium metal in the lower part of the furnace and the sample in the upper part.[9] The sample and the potassium temperatures were (i) $T_s = 230\,^\circ C$ and $T_K = 130\,^\circ C$ in one experiment and (ii) $T_s = 320\,^\circ C$ and $T_K = 250\,^\circ C$ in a separate experiment. The potassium vapor pressure, p_K was estimated from the value of T_K as $p_K = 0.002$ Torr at $T_K = 130\,^\circ C$ and $p_K = 0.057$ Torr at $T_K = 250\,^\circ C$.[10] All x-ray scans reported on here are confined to the $(00l)$ reflections. We used Mo $K\alpha$ radiation monochromated by a flat graphite monochromator in the incident beam.

III. RESULTS AND DISCUSSION

Figure 1 shows a sequence of $(00l)$ reflections taken during the sequential intercalation process of potassium atoms into the stage-2 $CoCl_2$ GIC with $T_K = 130\,^\circ C$ and $T_s = 230\,^\circ C$. The patterns of Fig. 1 are indexed with the notation $nI(00l)$, where n is the stage number, l is the order of the c-axis reflection and I denotes the intercalant species: I=Co for $CoCl_2$-GIC, H for $CoCl_2$-K GIC and K for K GIC. For 3 h, we find two reflections corre-

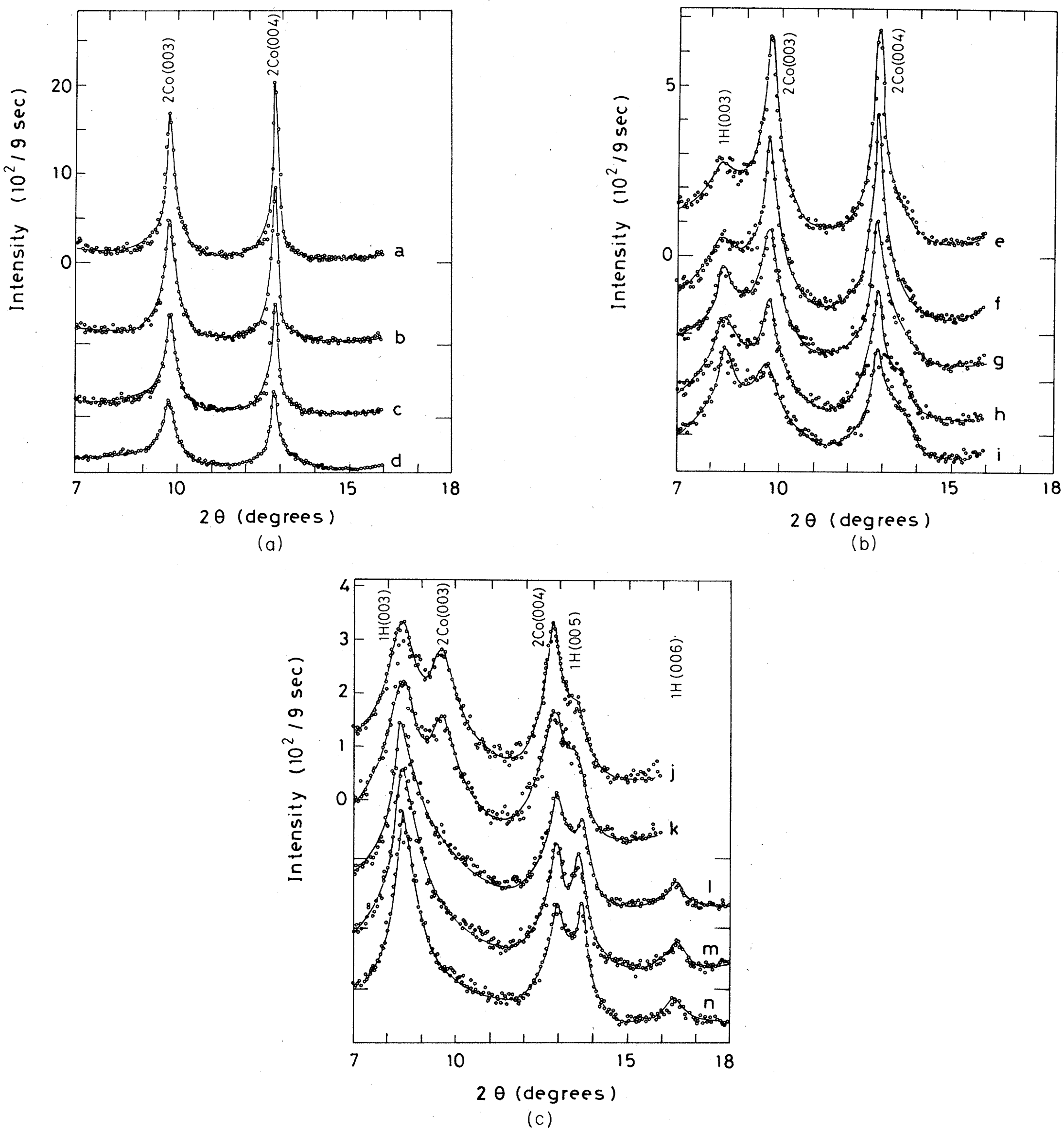

FIG. 1. Variation of (00*l*) diffraction pattern with time during the sequential intercalation of potassium atoms into stage-2 $CoCl_2$ GIC based on single crystal of Kish graphite. We used *in situ* x-ray diffraction with Mo $K\alpha$ radiation. The temperature of the stage-2 $CoCl_2$ GIC and the potassium were kept at $T_s = 230\,^\circ\mathrm{C}$ and $T_K = 130\,^\circ\mathrm{C}$, respectively. The reflections labeled $1H(00l)$ and $2\mathrm{Co}(00l)$ correspond to stage-1 heterostructure $CoCl_2$-K GIC and stage-2 $CoCl_2$ GIC. The curves are labeled as follows (with accompanying *t* values in units of hours). (a) *a*, 0.4; *b*, 1.3; *c*, 2.2; *d*, 4.0. (b) *e*, 5.0; *f*, 5.5; *g*, 7.1; *h*, 8.6; *i*, 10.2. (c) *j*, 11.2; *k*, 12.2; *l*, 23.4; *m*, 29.3; *n*, 34.1. The solid lines are guides to the eye.

sponding to 2Co(003) and 2Co(004) of the stage-2 $CoCl_2$ GIC which appear at $2\theta = 9.67^\circ$ and 12.90° [Fig. 1(a)]. The repeat distance is $d_0 = 12.65$ Å. These Bragg peak intensities decrease with time. After 3 h, a new Bragg reflection appears at $2\theta = 8.34^\circ$ [Fig. 1(b)]. This reflection corresponds to the $1H(003)$ of the stage-1 heterostructure $CoCl_2$-K GIC with a *c*-axis stacking sequence C-$CoCl_2$-C-K-$CoCl_2$-C-K-C-$\cdots$ and an interplanar spacing $d_H = d_1 + d_2 = 14.65$ Å, where $d_1 = 9.30$ Å is the C-$CoCl_2$-C stack thickness and $d_2 = 5.35$ Å is the C-K-C stack thickness. After 6 h, the reflection $1H(005)$ appears at $2\theta = 13.93^\circ$, and the heterostructure peaks gradually increase at the expense of the stage-2 $CoCl_2$ GIC peaks. In Fig. 2, we plot the time dependence of the peak intensities of the $1H(003)$ and 2Co(004) reflections. After 10 h, the intensity of the $1H(003)$ peak becomes larger than the 2Co(004) peak. After 13 h, accurate intensity measurements are not possible any more because of overlapping peaks and possible increase of the sample mosaic. Finally, the 2Co(003) reflection disappears, and after 45 h we find only the $1H(003)$, $1H(005)$, $1H(006)$, and 2Co(004) reflections, which then remain stable. Note that we do not observe a $1H(004)$ reflection. At 45 h, the intensity ratio of the $1H(003)$ to the 2Co(004) reflection is roughly 1.6.

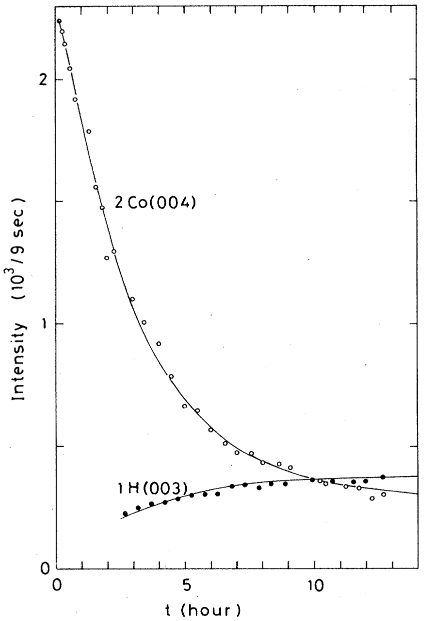

FIG. 2. Time dependence of the x-ray peak intensities of the reflections $1H(003)$ and 2Co(004) during *in situ* preparation. The solid line is a guide to the eye.

The rapid decrease of the 2Co(003) peak intensity may be related to the fact the linewidth of the 2Co(003) reflection is larger than that of 2Co(004) reflection in the staring stage-2 $CoCl_2$-GIC sample. This indicates some disorder in the distribution of the $CoCl_2$ intercalate and the graphite host layers. The disorder along the c axis is a general characteristic of the acceptor-type GIC's with smaller charge transfer than the donor-type GIC's.[11] As is deduced from the study on $FeCl_3$ GIC by Metz and Hohlwein,[12] based on a Hendricks-Teller analysis[13] only the $(0\,0n+2)$ reflection of the stage-n $CoCl_2$GIC remains sharp irrespective of the c-axis stacking disorder.

To confirm the stacking sequence of the stage-1 heterostructure $CoCl_2$-K GIC we calculated the $(00l)$ x-ray intensities of the pure stage-2 $CoCl_2$ GIC and the stage-1 heterostructure $CoCl_2$-K GIC.[14] In the stage-2 $CoCl_2$ GIC we assume the following sequence of layers along the c axis: carbon, chlorine, cobalt, chlorine, carbon, and carbon. The squared amplitudes of the structure factor for x rays scattered from the stage-2 $CoCl_2$ GIC and the stage-1 heterostructure $CoCl_2$-K GIC can be given by

$$\left|S_{\mathrm{Co}}(Q_c)\right|^2=|S_0|^2\sum_l \delta\left[Q_c-\frac{2\pi l}{c_0+2c_1}\right] \times \left|pf_{\mathrm{C}}+pf_{\mathrm{C}}e^{iQ_c c_0}+qf_{\mathrm{Cl}}e^{iQ_c(c_0+c_1-z_0)} +qf_{\mathrm{Cl}}e^{iQ_c(c_0+c_1+z_0)}+qf_{\mathrm{Co}}e^{iQ(c_0+c_1)}\right|^2, \tag{1}$$

and

$$|S_H(Q_c)|^2=|S_0|^2\sum_l \delta\left[Q_c-\frac{\pi l}{c_1+c_2}\right] \times \left|pf_{\mathrm{C}}+rf_{\mathrm{K}}e^{iQ_c c_2}+pf_{\mathrm{C}}e^{iQ_c 2c_2} +qf_{\mathrm{Cl}}e^{iQ_c(2c_2+c_1-z_0)}+qf_{\mathrm{Cl}}e^{iQ_c(2c_2+c_1+z_0)} +qf_{\mathrm{Co}}e^{iQ_c(2c_2+c_1)}\right|^2, \tag{2}$$

where $|S_0|^2$ is a constant, Q_c is the component of the wave vector $\mathbf{Q}$ along the c axis, f_x is the atomic form factor of the x species, which is assumed to be independent of Q_c, z_0 is the distance between the cobalt and the chlorine layers ($z_0=1.41$ Å), c_0, $2c_1$, and $2c_2$ are the repeat distances of pure graphite, stage-1 $CoCl_2$ GIC's and C_8K, respectively ($c_0=3.35$ Å, $d_1=2c_1=9.30$ Å, $d_2=2c_2=5.53$ Å), and $d_0=c_0+2c_1$ ($=12.65$ Å) for stage-2 $CoCl_2$ GIC's, p, q, r, respectively, are the numbers of carbon, cobalt (chlorine), and potassium atoms per unit area:

$$p=\frac{4}{(3a^2)^{1/2}}=0.39,\quad q=\frac{2}{(3b^2)^{1/2}}=0.09\,,$$

a and b are the in-plane lattice constants of graphite and $CoCl_2$. Figure 3 shows the calculated diffraction pattern for the ideal stage-1 heterostructure $CoCl_2$-K GIC [Fig. 3(a)] and the ideal stage-2 $CoCl_2$ GIC [Fig. 3(b)], where $r=p/12$ is chosen as the same in-plane concentration as $C_{12}K$ and $Q_c=(4\pi/\lambda)\sin\theta$, $\lambda=0.71073$ Å. If we assume the in-plane concentration of K atoms in the potassium layer of the heterostructure to correspond to that of $C_{12}K$ or $C_{14}K$, the square of the structure factor for the $1H(003)$ peak is larger than that of the $1H(005)$. For an in-plane concentration corresponding to C_8K the intensities are reversed.

As evident from Fig. 3, the peak intensities of the $1H(003)$, $1H(005)$, and $1H(006)$ reflections in Fig. 3(a) and 2Co(003) and 2Co(004) reflections in Fig. 3(b) are very strong compared to the other reflections, which is in excellent agreement with the experimental results. As mentioned before, after 34 h of K intercalation there remains only the Bragg reflections $1H(003)$, $1H(005)$, $1H(006)$, and 2Co(004). We also notice that the peak intensity of the $1H(003)$ reflection is larger than that of the $1H(005)$ reflection. This result indicates that (i) part of stage-2 $CoCl_2$ GIC's is replaced by the stage-1 heterostructure $CoCl_2$-K GIC and that (ii) the in-plane concentration of the potassium layer is close to that of $C_{12}K$ or $C_{14}K$ rather than C_8K. In a more accurate[1] structure factor analysis one would need to take the $\mathbf{Q}$ dependence of the atomic form factors as well as polarization and Lorentz factors into account. However, one may still not obtain an ideal fit to the measured intensities because of the stacking disorder and the change of the mosaic spread during the intercalation process. The present analysis therefore serves only the purpose to demonstrate on a more qualitative basis the existence of a stage-1 donor-acceptor heterostructure and its coexistence with a remaining stage-2 $CoCl_2$ GIC.

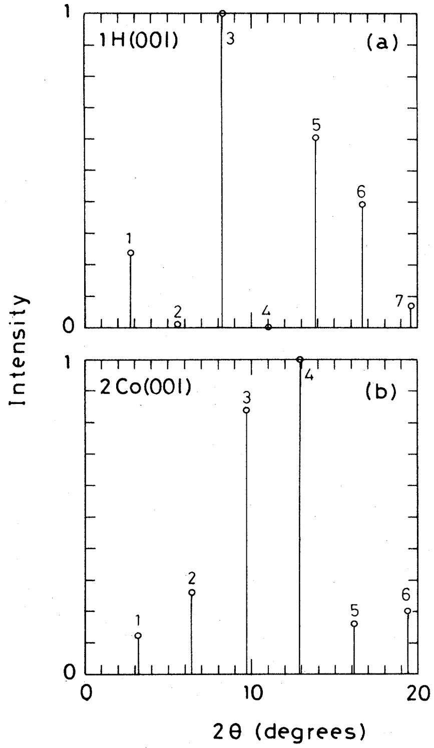

FIG. 3. Structure factor calculations of the Bragg intensities of the reflections $1H(00l)$ for the stage-1 heterostructure $CoCl_2$-K GIC (repeat distance $d_H = 14.65$ Å) and $2Co(00l)$ for stage-2 $CoCl_2$ GIC ($d_0 = 12.65$ Å). The intensities of $1H(00l)$ and $2Co(00l)$ are normalized by those of $1H(003)$ and 2Co(004), respectively. $I(2Co(004)/I(1H(003)) = 0.70$. The potassium layers are assumed to have the same in-plane concentration as the stage-2 K GIC, $C_{24}K$.

From the structure factor calculation above we obtain for the ratio of the $1H(003)$ to the 2Co(004) intensities a factor of 1.43 which compares to the experimental value of 1.6. Thus, the final product consists of a mixture of a stage-1 C-$CoCl_2$-C-K-C heterostructure and a stage-2 $CoCl_2$ GIC with a ratio of roughly 1:1. The coexistence of the two different compounds in equilibrium may be understood in terms of the Daumas-Hérold model.[6] In this model it is assumed that domains of intercalant atoms are present between any graphite layers, and a stage-*n* compound then consists of *n* different types of domains. In the stage-2 $CoCl_2$ GIC we assume two kinds of domains (*A* and *B*) as shown in Fig. 4. The potassium atoms pass through empty galleries between adjacent graphite layers from the crystalline edge to the boundary of the other domain. When the vapor pressure p_K is sufficiently low, the potassium atoms do not proceed to the same gallery of the adjacent domain which is occupied by $CoCl_2$ molecules. As is schematically shown in Fig. 4(b), we then expect the sample to be composed of domains with the stage-1 heterostructure $CoCl_2$-K GIC (*A*1,*B*1) and domains with stage-2 $CoCl_2$ GIC (*A*2,*B*2). The appearance of domains with different repeat distances may cause stacking disorder and/or stress in the domain boundary, which causes diffuse scattering and broadening of the Bragg reflections, respectively, although we have not noticed a variation of the width of (00*l*) reflections with time.

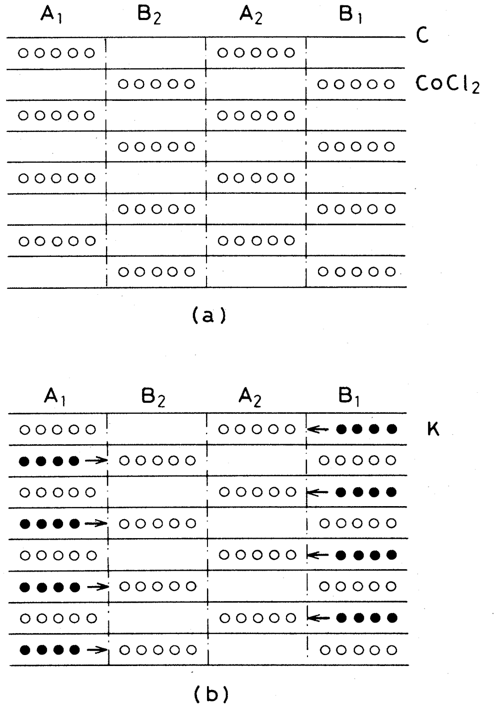

FIG. 4. (a) Daumas-Hérold model for the stage-2 $CoCl_2$ GIC with domains, *A* and *B*. (b) Possible structure after the sequential intercalation of potassium atoms into the stage-2 $CoCl_2$ GIC, where the potassium atoms are not assumed to move from *A*1 to *B*2, or from *B*1 to *A*2.

We have also grown a heterostructure compound by the sequential intercalation technique at the temperatures $T_s = 320\,^\circ C$ and $T_K = 250\,^\circ C$ of the sample and alkali-metal furnace, respectively. At these higher temperatures the outside alkali-vapor pressure and the alkali diffusivity within the sample are increased. Within 10 min the $1H(003)$ and $1H(005)$ reflections appear [Fig. 5(a)] and the peak intensities reach their maxima, while the 2Co(003) reflection disappears completely. The 2Co(004) peak intensity rapidly decreases to $\frac{1}{10}$ of that before intercalation, and thereafter remains unchanged. But the position shifts to a higher angle $2\theta = 13.1^\circ$ after 8 h. This corresponds to the 1Co(003) position which remains sharp among the 1Co(00*l*) reflections of the stage-1 $CoCl_2$ GIC. This result suggests the occurrence of a stage transformation from stage 2 to stage 1 in part of the $CoCl_2$ GIC. On the other hand, the $1H(003)$ and $1H(005)$ peak intensities gradually decrease and disappear completely after 8 h [Fig. 5(b)]. After 13 h, the 1K(001) and 1K(002) reflections of the stage-1 K GIC appear. The peak intensities of 1K(001) and 1K(002) grow with the time and are saturated after 40 h [Fig. 5(c)] while the peak intensity of 1Co(003) remains unchanged after 8 h onward. The sample is therefore finally composed of a stage-1 K GIC and a stage-1 $CoCl_2$

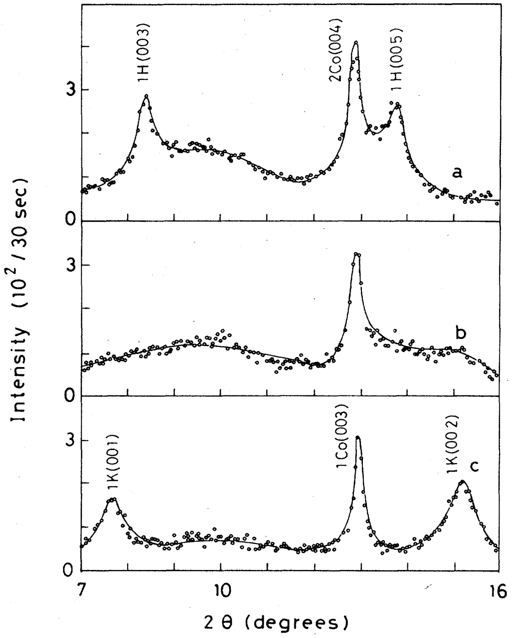

FIG. 5. Variation of $(00l)$ x-ray diffraction pattern with time during the sequential intercalation of potassium atoms into stage-2 CoCl_2 GIC. Here, the temperatures are $T_s = 320\,^\circ\mathrm{C}$ and $T_{\mathrm{K}} = 250\,^\circ\mathrm{C}$ for the sample and K furnace, respectively. The reflections labeled $1H(00l)$, $1\mathrm{K}(00l)$, $1\mathrm{Co}(00l)$, and $2\mathrm{Co}(00l)$ correspond to stage-1 heterostructure CoCl_2-K GIC, stage-1 K GIC, stage-1 CoCl_2 GIC, and stage-2 CoCl_2 GIC, respectively. *a* is $t = 10$ min, *b* is 8 h, *c* is 45 h. The solid lines are guides to the eye.

GIC, again in a ratio of roughly 1:1. The kinetics can also be explained by the Daumas-Hérold model. In this case the CoCl_2 molecules in the domains $A1$ and $B1$ of Fig. 4(b) near the crystallite edge move to the empty galleries in the $B2$ and $A2$ domains, respectively, because of the high alkali-vapor pressure. Then the domains $A1$ and $B1$ change from stage-1 heterostructure CoCl_2-K GIC to a stage-1 K GIC and the domains $A2$ and $B2$ change from stage-2 CoCl_2 GIC's to stage-1 CoCl_2 GIC's.

From the present experience with the sequential intercalation of potassium into a stage-2 CoCl_2 GIC, we conclude that a similar intercalation of K in a stage-n CoCl_2 GIC may give rise to $n-1$ different kinds of heterostructures. For example, in the case of $n=4$, we may get a novel GIC which is composed of three kinds of domains with the stacking sequences:

$$\mathrm{C\text{-}CoCl_2\text{-}C\text{-}K\text{-}C\text{-}K\text{-}C\text{-}K\text{-}C\text{-}CoCl_2\text{-}C}\ ,$$

$$\mathrm{C\text{-}CoCl_2\text{-}C\text{-}K\text{-}C\text{-}K\text{-}C\text{-}C\text{-}CoCl_2\text{-}C}\ ,$$

$$\mathrm{C\text{-}CoCl_2\text{-}C\text{-}K\text{-}C\text{-}C\text{-}C\text{-}CoCl_2\text{-}C}\ ,$$

in addition to

$$\mathrm{C\text{-}CoCl_2\text{-}C\text{-}C\text{-}C\text{-}C\text{-}CoCl_2\text{-}C}\ .$$

IV. CONCLUSION

The stage-1 heterostructure CoCl_2-K GIC was synthesized by the sequential intercalation of potassium atoms into stage-2 CoCl_2 GIC's. Part of the stage-2 CoCl_2 GIC near the sample edge transformed into stage-1 heterostructure CoCl_2 K GIC. The mechanism of sequential intercalation may be understood in terms of the Daumas-Hérold domain model. The present experimental results suggest the possibility that more complicated materials than stage-1 heterostructure GIC's may be synthesized by a variety of sequential intercalations.

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[14] It is likely to assume that the CoCl_2 layer in the heterostructure has a structure similar of that of CoCl_2 GIC. The in-plane structure of the CoCl_2 layer in the stage-2 CoCl_2 GIC was confirmed by electron diffraction to be incommensurate with graphite and to be rotated by 30° with respect to the graphite lattice. The CoCl_2 layer forms a triangular lattice with an in-plane lattice constant at $b = 3.57$ Å (see Ref. 8).