2 D-3 D TRANSITIONMULTILAYER ADSORPTION OF ARGON AND KRYPTON ON LAMELLAR HALIDES

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MULTILAYER ADSORPTION OF ARGON AND KRYPTON ON LAMELLAR HALIDES

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Résumé. — Des réseaux d'isothermes d'adsorption d'argon et de krypton sur la face de clivage de divers halogénures lamellaires ont été déterminés. Pour chaque couple adsorbat-adsorbant un nombre spécifique de couches monomoléculaires se forment au cours de condensations bidimensionnelles qui sont des transitions du premier ordre. Nous avons porté notre attention tout particulièrement sur l'entropie associée à ces transitions. Nous avons montré que le nombre de monocouches pouvant se former dépendait essentiellement de la compatibilité dimensionnelle entre adsorbat et adsorbant.

Abstract. — Sets of adsorption isotherms of argon and krypton on the cleavage face of a number of lamellar halides have been determined. For each adsorbate-adsorbent pair a specific number of adlayers are formed during two-dimensional condensations, which are first order transitions. Particular attention has been paid to the entropy associated with these transitions. The number of adlayers that can form has been shown to depend essentially on the dimensional incompatibility between adsorbate and adsorbent.

1. **Introduction.** — The experimental data presented and discussed in this paper concern the multilayer adsorption of argon and krypton on the cleavage face of lamellar dihalides. For these systems a number of sets of adsorption isotherms have been determined at temperatures below the triple point of the bulk adsorbate [1-3]. They clearly show that the adfilm is a stacking of physical monolayers, in the same way as bulk crystals of f.c.c. rare gases can be considered as stackings of their densest (111) crystallographic planes. As the gas pressure is increased monolayers are formed, one after the other, through first order transitions, including at least one two-dimensional (2 D) condensation for each layer (Fig. 1).

Nine years ago, one of us [4] developped a method of analysis of the data taking into account, at the outset, these crucial observations, which both the most popular theories of multilayer adsorption, the Brunauer, Emmett, Teller (B.E.T.) and the Frenkel, Hill, Halsey (F.H.H.) do not. Given the very unrealistic silhouette of a bombarded metropolis characteristic of a B.E.T. film [5] completely opposite to the experimental situation which we observe, we feel that starting from B.E.T. would be a most unnatural way of developing a theory of
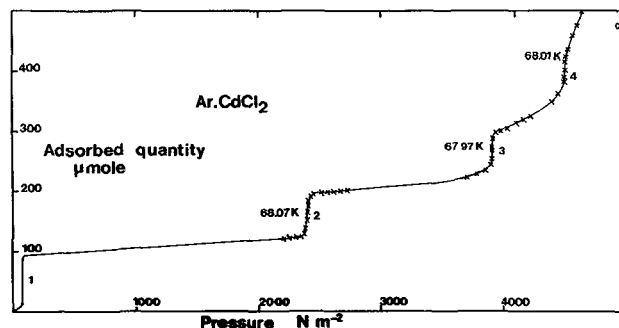
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Fig. 1. —Adsorption isotherm of argon on cadmium chloride. (Note that, each layer being studied independantly, the curve is not strictly isotherm.)

layer-like films. On the other hand there seems to be no insuperable hindrance for giving a layer-like character to the slab model of the F.H.H. theory (see Chapter 5 of [6]). Actually the major deficiency of the latter is that it has not yet been able to take into account surface structure which, at low temperature, has an outstanding effect on the properties of adfilms. We shall first briefly outline the original aspects of our method of analysis of sets of stepped adsorptions isotherms. Then we shall present and discuss our data. In view of their extent a thorough analysis cannot be considered in this space limited article. We have chosen to emphasise the analysis of entropy, neglecting other important

parameters such as the critical temperature, for instance.

2. **Theoretical.** — A set of adsorption isotherms appears as the representation of the (Γ, T, μ) equation of state of a one-component 2 D system, i.e. of the surface density $\Gamma = N/A$ versus the chemical potential μ at constant temperature T (for convenience, the adsorbed quantity N, at constant area A, is plotted against $\log p = (\mu - \mu^0)/RT$, where μ^0 is the chemical potential of the ideal gaseous adsorbate at unit pressure). Actually this is only true when the adsorbent is limited by a single homogeneous surface, for instance by a given crystalline face, in which case the adsorbent is called uniform. When various patches, having different structures, limit the adsorbent, a different equation of state of the adphase clearly corresponds to each of these and the set of adsorption isotherms yields only averages of physical quantities difficult to interpret [1, 7]. Interparticle condensation at high relative pressures, which occurs even for uniform adsorbents, also prevents one from obtaining data relating to a single type of surface.

Fortunately enough there is an important exception to this pessimistic statement. When first order transitions occur, the sets of adsorption isotherms have a monovariant domain in which the thermodynamic quantities correspond to the single homogeneous surface on which the transition takes place [1, 7]. If we add that the isosteric heat, a most important parameter in physical adsorption, can be measured with an accuracy much greater in the monovariant domain than in the bivariant one, we give two major reasons for emphasizing the analysis of the isotherms in the transition domain, as we have done from the beginning of our studies [8].

For two coexisting adphases, a dilute one' and a dense one", the transition pressure p at temperature T, obeys the following equations [1, 7] :

$$\frac{R \, d \, Ln \, p}{d \, 1/T} = \frac{\Gamma'' u'' - \Gamma' u'}{\Gamma'' - \Gamma'} - h^{(g)} \qquad (1)$$

$$R \, Ln \, p = \left(\frac{\Gamma'' u'' - \Gamma' u'}{\Gamma'' - \Gamma'} - h^{(g)}\right)\bigg/ T + s_0^{(g)} -$$

$$- \frac{\Gamma'' s'' - \Gamma' s'}{\Gamma'' - \Gamma'} \qquad (2)$$

u and s are the molar internal energy and entropy ; Γ is the surface density ; $h^{(g)}$ and $s_0^{(g)}$ are the molar enthalpy and entropy of the bulk gaseous phase, supposed ideal, at unit pressure.

At first sight the two energetic and entropic parameters of these equations do not look simple. Fortunately enough, when the observed transition is a 2 D condensation in an nth layer — in which case we write $(\Gamma'' u'' - \Gamma' u')/(\Gamma'' - \Gamma') = u^{(n)}$ and $(\Gamma'' s'' - \Gamma' s')/(\Gamma'' - \Gamma') = s^{(n)}$ — they can be considered as giving estimates of the internal energy

and entropy of the nth dense layer formed during the transition in a hypothetical state in which its vacancies would have been filled up. We must stress that this statement is supported only by plausibility arguments [1, 9, 10]. Moreover there is a significant restriction : $u^{(n)}$ and $s^{(n)}$ have no simple meanings if the 2 D condensation in the nth layer produces important changes in the $(n - 1)$ underlying ones. Clearly this point should be looked at very carefully in each specific case.

With $u^{(n)}$ and $s^{(n)}$ we naturally associate

$$f^{(n)} = u^{(n)} - Ts^{(n)} \qquad (3)$$

the molar Helmholtz free energy of an nth layer.

The outer densest plane of a bulk crystal, the (111) plane for rare gases, can be considered as an adlayer at an infinite distance from an adsorbent. For such a plane we define $u^{(\infty)}$ and $f^{(\infty)}$ which will be related to the saturation pressure $p^{(\infty)}$ of the bulk adsorbate in the same way as $u^{(n)}$, $s^{(n)}$ and $f^{(n)}$ are related to $p^{(n)}$, so that we can write :

$$R \frac{d \, Ln \, p^{(\infty)}/p^{(n)}}{d \, 1/T} = u^{(\infty)} - u^{(n)} \qquad (4)$$

$$R \, Ln \, p^{(\infty)}/p^{(n)} = (u^{(\infty)} - u^{(n)})/T + s^{(n)} - s^{(\infty)} . \qquad (5)$$

Equation (5), which one of us first introduced in 1968 [4], clearly shows the main shortcoming of the F.H.H. equation, in which one implicitly admits $s^{(n)} - s^{(\infty)} = 0$. Not only can this entropic term be as important as the energetic one [8], but also experimental situations have been encountered in which a layer exists although it is energetically unstable $(u^{(\infty)} - u^{(n)} < 0)$ because of its comparatively high entropy [11]. Now, of course, it remains to interpret the entropy differences $s^{(n)} - s^{(\infty)}$.

3. **Experimental results. Discussion.** — 3.1 A PERFECTLY COMPATIBLE SYSTEM. — The cleavage plane of lamellar dihalides is a triangular arrangment of halide ions having the same structure as the (111) plane of a bulk rare gas solid. In the particular case of the Ar-CdCl$_2$ system the crystalline parameters are exactly the same, so that we have an ideal situation for an epitaxial growth of argon monolayers over a layer of chloride ions. Experimentally we easily observe (Fig. 1) the formation of four layers. Each one has been studied in detail. A set of adsorption isotherms in the domain of formation of the third layer is given in figure 2. The experimental values of $s^{(n)} - s^{(\infty)}$ and $f^{(n)} - f^{(\infty)}$ are given in table I.

From the 2nd layer onwards the difference $(s^{(n)} - s^{(\infty)})/s^{(\infty)}$ is negligible. This is an expected result since we conjectured that the successive layers should have the same structure and the same crystalline parameter as the (111) planes of bulk crystalline argon and since the force field of the
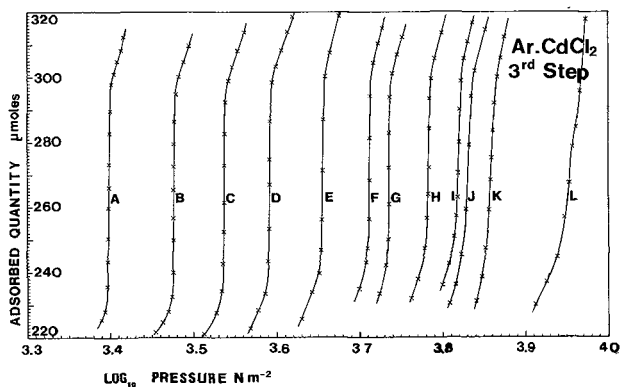
FIG. 2. — Adsorption isotherms of argon on cadmium chloride. Formation of the 3rd layer. Temperatures/K : A 65.90 — B 66.72 — C 67.36 — D 67.97 — E 68.66 — F 69.29 — G 69.58 — H 70.11 — I 70.54 — J 70.67 — K 70.94 — L 72.24 —.

TABLE I

Entropy and Helmholtz free energy of argon on cadmium chloride

Layer n°	1	2	3	4
Temperature/K	75	70	68	68
$s^{(n)} - s^{(\infty)}/J.K^{-1}.mol^{-1}$	− 4.16	0.21	−0.04	−0.33
$f^{(n)} - f^{(\infty)}/J.mol^{-1}$	− 2 375	− 411	− 121	− 46

$$s^{(\infty)} = 33 \text{ J. K}^{-1} \text{mol}^{-1}$$

$$h^{(g)} - h^{(\infty)} = 7 \text{ 960 J. mol}^{-1}$$

adsorbent manifests itself by a comparatively low extra energy for $n \geqslant 2$ as seen from table I. (In this table we give differences in Helmholtz free energies rather than in internal energies, since a much better precision is achieved in the measurement of the former and since both quantities are close to each other, the entropy differences being very low.) Clearly the contrary observation would have cast doubt on our interpretation of $s^{(n)}$. What might seem at first sight puzzling is the absence of a 5th layer. Using the R^{-3} law of decrease of energy with distance [6] we roughly estimate that it should occur at a relative pressure of 96 %. Given our experimental precision in pressure measurements and the uniformity of the temperature in the sample of adsorbent, the two-dimensional condensation in the 5th layer should manifest itself distinctly from the bulk condensation. However interparticle condensation can begin below the saturation pressure and prevent us from detecting a fifth step. We have previously given experimental evidence for such a phenomenon [11]. In the present study, the long time intervals needed to reach equilibrium at coverages above three layers and uncontrolled hysteresis observed above four layers are new indications for interparticle condensation. This means that the absence of steps above a relative

pressure of say about 90 % does not necessarily indicate that the number of adlayers is finite. In the present case, the entropy values strongly corrobate the more probable *a priori* hypothesis of a perfect epitaxial growth, i.e. of an infinite number of layers.

3.2 SYSTEMS HAVING A POSITIVE MISMATCH. — We define the mismatch between adsorbent and adsorbate as the relative difference between the parameters of the cleavage face of the former, a, and of the (111) plane of the latter, d [1]. We also call this quantity, which we write, $i = (a - d)/d$, the dimensional incompatibility. In figure 3 entropy differences $s^{(1)} - s^{(\infty)}$ are plotted against the dimensional incompatibility for argon and krypton on a number of lamellar halides of varying parameter a [1-3]. We look first at positive values of i.
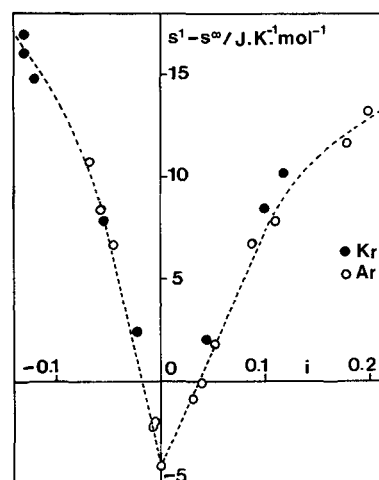

FIG. 3. — Variation of the entropy difference $s^{(1)} - s^{(\infty)}$ with the dimensional incompatibility i.

Up to about $i = 12$ % we have a linear variation of $s^{(1)} - s^{(\infty)}$ with i. For argon

$$s^{(1)} - s^{(\infty)} = 110 \, i - 4.16 \text{ J. K}^{-1} \text{mol}^{-1} . \quad (6)$$

Expanding a bulk crystal of argon by i^3, at constant temperature, results in an entropy increase which at first order may be writen

$$\Delta s = 3(\alpha v / \chi) \, i = 195 \text{ J. K}^{-1} \text{mol}^{-1} \quad (7)$$

α, v and χ are the expansion coefficient, the molar volume and the isothermal compressibility of solid argon [12]. A first adlayer of argon in perfect registry with the surface would be a (111) plane of bulk crystalline argon expanded by i^2. This is indeed strongly suggested by the fact that the coefficient of i in eq. (6) is about one half of that in eq. (7). A similar conclusion is valid for krypton [1, 2].

Since we cannot expect the relation between $s^{(1)} - s^{(\infty)}$ and i to remain linear up to 18 %, the deviation to linearity, observed for the Ar-CaI$_2$ and Ar-PbI$_2$ systems at $i = 17.9$ % and 19.9 %, cannot

be taken as a proof that no registered layer is formed at such incompatibilities. This remains an open question.

Of course, to the entropy increase with the dimensional incompatibility corresponds a heightening of the energy $u^{(1)}$ [1-3] since the adatoms are in positions less and less favorable for their lateral interactions.

The fact that for $0 \leq i \leq 0.12$, the first adlayer formed during the 2 D condensation is in perfect registry with the surface would seem to constitute a particularly simple situation for the study of the building up of the next layers. Actually this is not the case, since this first adlayer can change before the formation of the second one. Clearly the a priori probability of such an event increases with the deviation from compactness of the adlayer, i.e. when i increases. We have an illustration of such an effect in figure 4 : from the end of the transition (point A) to the classical B point a steep increase of the layer density is observed for the Kr-PbI$_2$ system at $i = 11.8$ %, while almost no change occurs for the perfectly compatible Ar-CdCl$_2$ system. Filling up of vacancies is insufficient to explain the density difference between B and A since the Kr-PbI$_2$ system is at more than 20 K below its critical temperature of 2 D condensation instead of 10 K for Ar-CdCl$_2$.
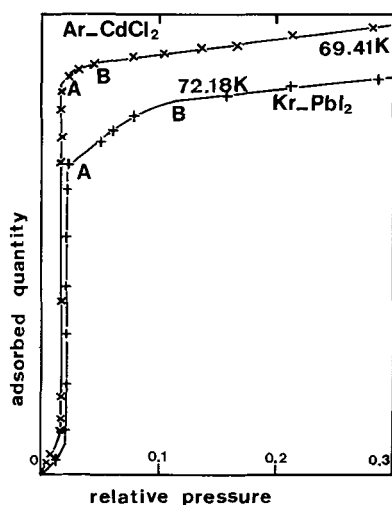

FIG. 4. — Behaviour of the first adlayer after the end of the transition.

A priori calculations of the potential energy of a rare gas atom on the cleavage face of a lamellar halide appears difficult [1-3]. But we can roughly estimate its variations as the adatom is moved over the surface, by choosing a similar but simpler system, for instance an argon atom over the (111) plane of a xenon crystal. According to Steele (page 37 of [6]) the promotion energies of an argon atom from a site to a saddle point or to a position above a xenon atom are respectively 74 and 288 K.

The structure variation of the adlayer of Kr on PbI$_2$ from A to B results from a tendancy towards close-packing as the surface pressure increases. The adatoms could leave the sites, we also call the potential wells, and adsord above saddle points but clearly not above the halide ions where the potential is too high. We imagine the structure of the adlayer in B as some kind of irregular close-packing, the adatoms standing around the path formed by the honeycomb lattice of the sites. Although such a structure might be more reminiscent of a liquid than of a crystal, we prefer to call it a solid, since potential barriers to translation will hinder the diffusive motion characteristic of a liquid.

Such an irregular and somewhat expanded adlayer will again be incompatible with the (111) plane of bulk adsorbate, and the incompatibility will tend to increase with i. From figure 5 we have a first clear indication of such a trend in the fact that, for $i \geq 0$, the entropy difference $s^{(2)} - s^{(\infty)}$ increases with the dimensional compatibility, although irregularly.
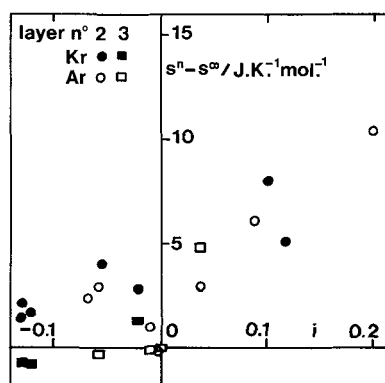

FIG. 5. — Variation of the entropy difference $s^{(n)} - s^{(\infty)}$ ($2 \leq n \leq 3$) with the dimensional incompatibility i.

Since the excess attraction energy due to the adsorbent has considerably diminished when one goes from the first to the second layer, as shown by table I for a perfectly compatible system, one easily imagines that for an incompatible one the lateral cohesion energy might become weak enough to make the second layer energetically instable compared to the (111) plane of bulk adsorbate. Actually this occurs as soon as the dimensional incompatibility becomes higher than about 8 % [1-3]. Second layers exist then only because of their high entropy and, according to eq. (5), will become unstable at low temperatures. For the Kr-CaI$_2$ system, at $i = 10.1$ %, eq. (5) writes [11] :

$$4.576 \log_{10} (p^{(\infty)}/p^{(2)}) = -134/T + 1.90$$

so that $p^{(2)}$ becomes higher than $p^{(\infty)}$ below 70 K. In that particular case, Larher and Haranger [11] effectively observed the disappearance of the second step of the adsorption isotherm around this

temperature. Most lamellar halides attracting the adatoms more than CaI_2 [13] the pressure at which $p^{(2)} = p^{(\infty)}$ is generally too low to permit the observation of the disappearance of the second layer.

The non negligible value of the entropy difference $s^{(3)} - s^{(\infty)}$ for the single 3rd layer observed at $i > 0$ for Ar on $CdBr_2$ suggests that an incompatibility still exists between the second layer and the (111) plane of bulk adsorbate. Now the attraction by the adsorbent has considerably diminished in a 3rd layer, as appears in table I, and might of course be insufficient to compensate the lack of lateral cohesion due to the incompatibility. Effectively, above $i = 3.9$ % (Ar-$CdBr_2$), no third layer is observed. One expects the formation of a 4th to be inhibited at even lower incompatibilities. The relatively high entropy of the 3rd layer of Ar on $CdBr_2$ makes very improbable the existence of a 4th which, at any rate, could not be detected because of interparticle condensation.

3.3 SYSTEMS WITH A NEGATIVE MISMATCH. —

The entropy curve (Fig. 3) $s^{(1)} - s^{(\infty)}$ vs i shows an angular point at $i = 0$. This means a change in structure at negative incompatibilities. Clearly the potential wells are not deep enough to permit a compressed (111) layer in simple registry with the surface. The important entropy increase as i decreases (for $i < 0$) probably arises from both a density decrease and a disordering of the first adlayer formed during the 2 D condensation. Again there is evidence [1-3] for a subsequent increase in the density up to the B point.

Figure 5 shows that the values of $s^{(n)} - s^{(\infty)}$ are generally low for $i < 0$ and $n \geq 2$. As the distance between the halide ions decreases, the surface appears smoother and smoother to the adatoms, so that the structure of the adlayer at point B could become closer and closer to that of the (111) plane of bulk adsorbate. This is one possible reason for the relatively low values of $s^{(2)} - s^{(\infty)}$.

A second observation, in good agreement with the first one, is that the number of adlayers is relatively high at $i < 0$: three for Kr on $NiCl_2$, $FeCl_2$, $CdBr_2$ [1] and for Ar on $FeCl_2$ and $MgBr_2$ [3]. In these five cases the non-observation of a 4th layer should not be considered as significant since it should normally appear at a relative pressure higher than 90 %. On the contrary, for these systems, an epitaxial growth

of an infinite number of layers would probably occur in the absence of interparticle condensation.

We note that the absence of a 3rd layer for the Kr-$CdCl_2$ system is again associated with a relatively high value of $s^{(2)} - s^{(\infty)}$.

4. **Conclusion.** — Stepped isotherms are characteristic of adsorption on uniform adsorbents. Perhaps the more striking outcome of this study is that, although we have been working on a set of systems showing great similarities, we find out that, in each particular case, a specific number of layers is formed. There is clear evidence that one of the main parameter on which this number depends is the dimensional incompatibility between the adsorbate and the adsorbent. This influence is particularly visible at positive incompatibilities for which one expects the locking by the surface of the first adlayer in B to be the more efficient, so that the incompatibility can transmit by simple contact to upper layers.

We find that, for $n \geq 2$, high values of the entropy differences $s^{(n)} - s^{(\infty)}$ are indicative of a limited number of layers. Unfortunately the range of application of this rule seems limited. A striking exception is constituted by the krypton-graphite system for which we find, for $s^{(2)} - s^{(\infty)}$, at 85 K, the rather high value of 3.6 $J.K^{-1}.mol^{-1}$, in good agreement with the estimate of Putnam and Fort [14]. Since five layers of krypton are observed on graphite [15], we suggest that epitaxial growth easily occurs for this system. The cleavage face of graphite is known to be a very smooth surface (see page 51 of [6]) so that at point B the first layer is only poorly locked to the surface. The mutual locking of two adlayers in contact is clearly much better, so that, there a high a $priori$ probability of finding two adlayers in mutual registry. This involves a change in the first as the second appears. Is that change responsible for the high value of $s^{(2)} - s^{(\infty)}$? Since low values of $s^{(2)} - s^{(\infty)}$ are associated to a large number of layers for Ar and Kr on lamellar halides at $i < 0$, should we conclude that such a process never happens on lamellar halides ? These are still open questions demanding new experiments.

The adsorption of the quasispherical molecule of methane [16], which lack of space has prevented us from discussing in this paper, again raises new embarrassing questions.

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DISCUSSION

J. ROUQUEROL. — In your paper you are writing that « new embarrassing questions » are raised by the adsorption of methane : could you give us an idea of these ?

Y. LARHER. — For the adsorption of methane, we find large values of $s^{(n)} - s^{(\infty)}$ for $n \geq 2$, and nevertheless a large number of layers can form, contrary to what we observe for rare gases. The explanation might be that for CH_4 the work was done at temperatures much closer to the bulk triple point than for rare gases.

M. SCHICK. — You have said that no registered adlayer exists at negative incompatibilities. Is it because you do not observe 2 D condensation ?

Y. LARHER. — We observe 2 D condensation at negative incompatibilities. If the adlayers were registered, their entropies would decrease as the dimensional incompatibility diminishes, which is contrary to the experimental observations.

W. STEELE. — Were these observations made at temperatures well below the bulk triple point temperature ?

Y. LARHER. — Yes.

M. BIENFAIT. — Did you observe registered structure in the same system by neutron scattering ?

Y. LARHER. — Yes, we observed a registered monolayer of ^{36}Ar on the cleavage face of MnI_2. This system has a dimensional incompatibility of 8 %.