PHYSICAL REVIEW E **80**, 031910 (2009)

Scale coloration change following water absorption in the beetle *Hoplia coerulea* (Coleoptera)

Marie Rassart,[*] Priscilla Simonis, Annick Bay, Olivier Deparis, and Jean Pol Vigneron
Research Center in Physics of Matter and Radiation (PMR), University of Namur (FUNDP),
61 rue de Bruxelles, B-5000 Namur, Belgium

(Received 21 April 2009; published 21 September 2009)

The blue scales on the cuticle of the male beetle *Hoplia coerulea* can absorb water, with the consequence that these scales, which have been shown to be responsible for the beetle's bright blue coloration, reversibly turn to emerald green with increasing water contents. Optical measurements are shown, by analytic photonic-crystal models, to be compatible with the full filling of the scales structures with water. The natural mechanism shows the way to produce a very efficient *hygrochromic* material: a medium which significantly changes color when its water contents are modified.

DOI: 10.1103/PhysRevE.80.031910 PACS number(s): 42.66.−p, 42.70.Qs, 42.81.Qb

I. INTRODUCTION

Insects have often developed very bright colors for different reasons, most often related to inter or intraspecies communication. Chemical defense protection is often more efficient when the appearance of the animal can easily be memorized: educated predators—who have tried eating a sacrificed individual—will generally not make a second attempt if the species is easily recognized. Conspicuous colors with possibly characteristic patterns can then help protecting an "unpalatable" species. For others, the coloration helps individuals to attract attention of the opposite sex, thereby improving the chances of a particular male to transmit its genetic patrimony. The male *Hoplia coerulea* displays a vivid blue color. The picture in Fig. 1, showing both a blue male and a (slightly larger) darker female, has been taken near the end of a sunny afternoon. Many male blue beetles were at that moment distributed at the upper end of bushes growing in a rather humid place on the bank of a stream. The small blue spots were visible from several tens of meters under a bright sun. The adult males adopt a strange position holding the stem with the two pairs of forelegs and lifting the large rear legs, waiting seemingly for a female inspection. Eventually, the dark heavy female appears, flies for about one or two minutes over the exposed males and suddenly dives straight on the stem occupied by one of them.

Most likely, the blue coloration plays a role in the choice made by the female, as the motion toward the chosen male starts several meters away from its sitting place, from where the colored visual signal is best perceived. It is however difficult, without biological field experiments, to know whether the driving force of the evolution toward a conspicuous sky-blue coloration for the male is the result of a better visibility from a distance or of a complex sexual color selection by the female, as was shown to happen with many other animals [1].

The blue coloration of the male has been shown to be associated with the internal structure of the scales which cover the upper part of the body of the insect, head, prothorax, and elytra. Pictures of this internal structure already appears in the book by Berthier [2,3] and the optical properties of this structure were analyzed quantitatively by Vigneron *et al.* [4]

In the present paper, compared to these earlier reports, is the serendipitous observation that the beetle actually changes color from blue to green when the cuticle is exposed to a prolongated contact with liquid water. This hygrochromic behavior was first observed on a dead specimen inadvertently presented in a wet glass vial. The coloring structure of *Hoplia coerulea* is known to leave some empty space where water can infiltrate. The replacement of air by water actually increases the average refractive index of the structure and increases the wavelength at which the Bragg-mirror gap occurs, changing the coloration from blue to green, as estimations will show in a moment. Experiment shows that the change of color also happens when the dry insect is exposed to a flow of water vapor: in this case, only the exposed side of the animal turns green.

The phenomenon is reversible: when drying, the insect upper cuticle fully restores its original bright blue coloration, scale by scale, in a manner described in Fig. 2. In the upper section of the figure, the insect scales have absorbed water and the head, back and elytra are uniformly green. In the lower section, the insect has been exposed to dry air for about ten minutes and has recovered a uniform blue. An interesting fact is that the blue coloration reappears by patches rather than through a gradual change of color.

The passive change of color of insects subjected to contact with water is not new: the large coleopter *Dynastes hercules*, for instance, is initially kaki-green when dry and turns to black when the surface of the cuticle is exposed to liquid water or to more than 80% humidity [5]. Though this change of coloration easily occurs on dead dry specimens, it is not so sure that, alive, this large *Dynastes* takes no active role in the control of the color transformation. As in some other hygrometry-sensitive structures in insects, humidity could be provided by internal sources. Little correlation, indeed, has been observed between the ambient hygrometry level and the beetle coloration on a living male specimen we have kept in the laboratory for about four months.

Active change of coloration from metallic gold to diffuse red is also seen on some tortoise beetles [6]. In these insects, a structural Bragg mirror which covers a pigmented red layer, can be switched on and off by changing from a struc-

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[*] marie.rassart@fundp.ac.be

FIG. 1. (Color online). *Hoplia coerulea*, male (above) and female (below) here photographed in the village of Meyras (Ardèche, France). The male is known for the spectacular blue coloration of the male. Viewing a female is an exceptional event, as it spends most of its time near the ground (in some descriptions, it was sometimes confused with the brown female of *Hoplia argentea*). The origin of the blue coloration of the male is the lamellar structure of the scales which covers the upper side of the insect's body. The female is dark, with some faint blue reflections, only visible in full sunshine (picture taken by one of the authors, J.P.V.).

tural order to disorder by way of varying the humidity contents.

Hoplia coerulea has not been reported to change color in the fields when alive and we have only observed this transformation on dry dead specimens. It is however true that the colonies of these insects are mostly found on soppy ground, near streams or even swamps (such as in the north of Spain). It is then tempting to speculate that, if the transformation occurs when the males are back to the ground—out of mating times—in the humid environment, it would make itself less conspicuous by changing its color to green. However, there is at present, to our knowledge, no observed support that the hygrochromic transformation occurs *in vivo*, in the insect's habitat.

This paper deals with the optical aspects of the hygrochromic behavior of the structure found in the insect's scales. We will first describe the reflectance measurements at different stages of water absorption and briefly recall the structure which explains the blue coloration. Models will then aim at explaining the change of optical properties as water replaces air in the structure. Finally, we will describe and provide interpretations for the peculiar way the multiscale structure found on the cuticle of the insect reaches dryness.

II. OPTICAL PROPERTIES

An Avaspec 2048/2 fiber-optic spectrophotometer with a combined equilibrated halogen-deuterium source covering somewhat more than the (human) visible spectral region was used for the measurements. We will only report specular measurements at a near-normal incidence and at a large angle, though intermediate angles have also been explored, without providing much more information. The reflected intensity is compared to the intensity scattered from a standard diffusive white polytetrafluoroethylene reference (Avaspec) in the same probe geometry. With this normalization, the reflected intensity is usually referred to as a "reflection factor," expressed in %. This quantity is not bound to be less than 100%.

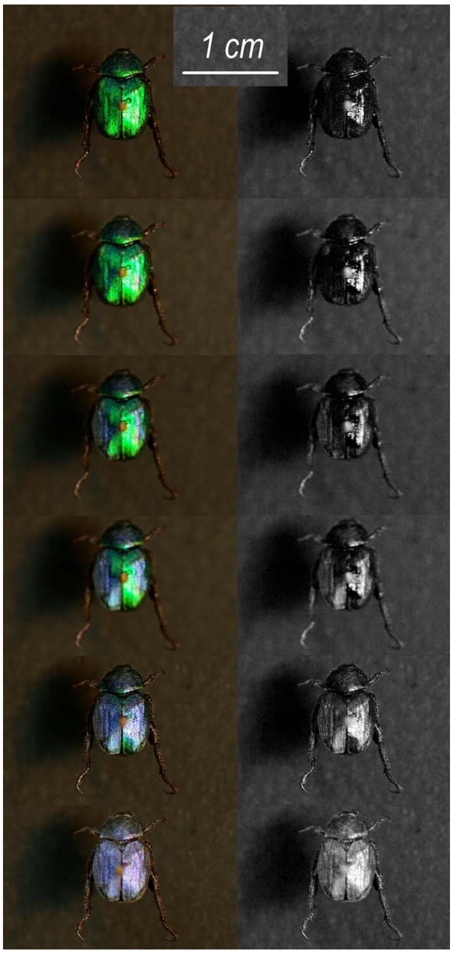

FIG. 2. (Color online) When brought to contact with water, the male *Hoplia coerulea* takes a bright emerald green coloration, following water absorption in the insect's scales. This coloration change is reversible. The figure shows, in two different forms (left and right), a series of pictures taken during the drying process, which took about 15 min (three minutes between pictures) of a specimen put in contact with water (top) and then left to dry (bottom). The left series is unprocessed, while in the right series, the pictures have been processed so than the green coloration appears dark, while the blue coloration appears lighter. It is observed that the blue coloration is recovered by growing patches.

The reflection factor was first measured on a wet elytron, glued on a glass slab, and cut in such a way that the sample could be flattened under a uniform pressure. The reflection was measured in a specular geometry (i.e., with equal incidence and emergence angles), at two incidence angles, 15° and 60°. The upper part of Fig. 3 gives the measured results for this "green" state of the insect, where the scales and cuticle surface are saturated with liquid water. The dominant wavelength near the normal incidence, $\theta=15°$ from the cuticle normal, is $\lambda=530$ nm. This dominant wavelength lies in the colorimetric area usually described as "yellowish-green," close to "green" [7,8].

When the angle of incidence and the probed emergence angles are both increased to $\theta=60°$, the dominant wave-

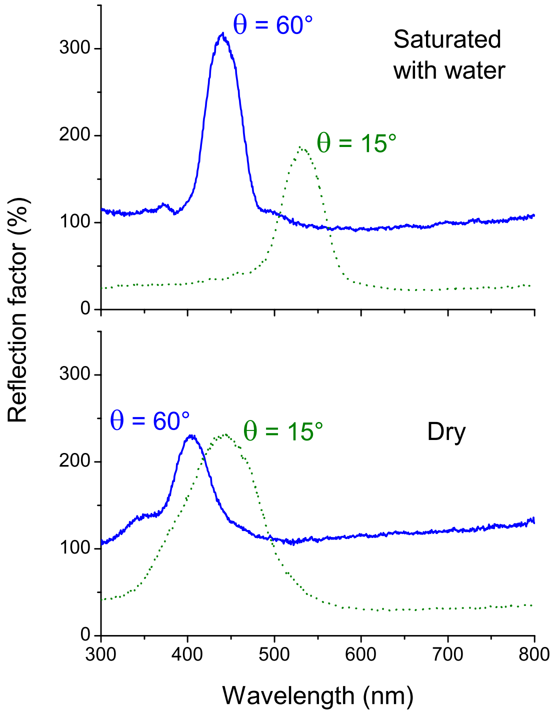

FIG. 3. (Color online). Reflection factor (specular intensity in units of the intensity scattered by a diffusive white standard in the same probe solid angle) of the cuticle of the beetle *Hoplia coerulea*, saturated with water (green near-normal incidence, above) and dried (blue near-normal incidence, below). The measurement was carried out in a specular mount (a symmetrical configuration with equal angles of incidence and emergence), at two incidence and emergence angles, $\theta=15°$ and $\theta=60°$, showing the iridescence in extreme cases of water contents.

length shifts to $\lambda=440$ nm, in a colorimetric zone described as "purplish blue" [7,8]. The shortening of the dominant reflected wavelength for increasing incidence angles is a well-known property of Bragg mirrors, referred to as "iridescence" [9].

The same piece of elytron was used, after about half an hour of exposition to dry air, to measure the optical reflection factor of the cuticle in its "blue" state. The result is shown in the lower part of Fig. 3, where the reflection factor is again shown for the incidences $\theta=15°$ and $\theta=60°$. At near-normal incidence, the dominant wavelength of the reflected light lies in the "purplish blue" [7,8] region, near $\lambda=450$ nm. This result agrees with the results obtained in an earlier publication dealing with different specimens of the same species [4]. At an incidence $\theta=60°$, the reflection peak shifts to $\lambda=400$ nm, in the "violet" spectral range, at the border of the human visible spectrum (admittedly 380 nm).

If, following Deparis [10,11], we define the "spectral richness" as the spectral shift of the dominant reflected wavelength as the angle is increased from normal to grazing incidence, we find that the spectral richness is larger for a water-saturated scale than for a dry scale. Deparis *et al.* [11] showed that the spectral richness was favored by small refractive index contrasts, and this argument can be applied here.

We also note the presence of a weak satellite peak, on the short-wavelength side of the main reflection, which was not noticed on previous optical measurements (see Ref. [4]). It should be noted that the insects used in the present study are not originating from the same location as those used earlier, so that slight differences of color could be expected. The coloration of a coleopter such as the European *Cetonia aurata*, for instance, can vary wildly (sometimes green, blue, red…), depending on its origin and on various development factors. All these variants pertain to the same species with fertile offspring in crossed breeding.

III. MORPHOLOGY AT THE LIGHT-WAVELENGTH SCALE

The blue coloration of dry specimens has been shown to be produced by a layered structure inside each of the scales (or squamae) of the male *Hoplia coerulea* [4]. In order to be reasonably comprehensive, we will briefly report again the results of this investigation, while mentioning the data relevant to the present study. Figure 4 shows a side (lower part) and a top (upper) view of the internal structure of a typical scale. The structure is a stack of a dozen layers all built from the same recipe: a thin flat slab of chitin wearing on one side parallel rods with a rectangular cross-section.

Dimensions of the different elements of the structure are known from Vigneron *et al.* [4] but, due to the different origin of the specimens under study, these dimensions have been reexamined, producing very slightly different results (Fig. 5). The thickness of the basal slab is $d=35$ nm and the height of the rods is $h=140$ nm, which makes a total vertical period of $a=d+h=175$ nm. The width of the lateral voids between the rods can be estimated to be close to $g=85$ nm, while the rods width is, on the average, $w=90$ nm, giving a lateral period (possibly providing diffraction) of $b=g+w=175$ nm.

It is believed that the material from which the rods and the basal slabs are made is chitin, with a refractive index, averaged over blue wavelengths of $n_c=1.6$ [12,13]. This corresponds to a dielectric constant $\varepsilon_c=2.56$. When a long-wavelength, nonpolarized light beam is incident on such an anisotropic structure, the effective dielectric constant is the average of its dielectric response functions for electric fields either oriented along the rods or across the rods. The voids have a dielectric function, in this state, $\varepsilon_v=1$. Following the arguments developed in [4], the former is obtained by calculating $\varepsilon_\parallel$ in

$$(g+w)\varepsilon_\parallel = g\varepsilon_v + w\varepsilon_c \tag{1}$$

(as in parallel electrostatic capacitors). The latter is obtained by calculating $\varepsilon_\perp$ in

$$\frac{g+w}{\varepsilon_\perp} = \frac{g}{\varepsilon_v} + \frac{w}{\varepsilon_c} \tag{2}$$

(as in a series arrangement of capacitors). These formula provide the following estimations of the dielectric tensor components: $\varepsilon_\parallel=1.80229$ and $\varepsilon_\perp=1.45644$. For unpolarized waves, the average response function of the rods layer would be $\varepsilon=1.62936$. For the whole structure, including the solid chitin basal slab, a formula similar to Eq. (1), namely,

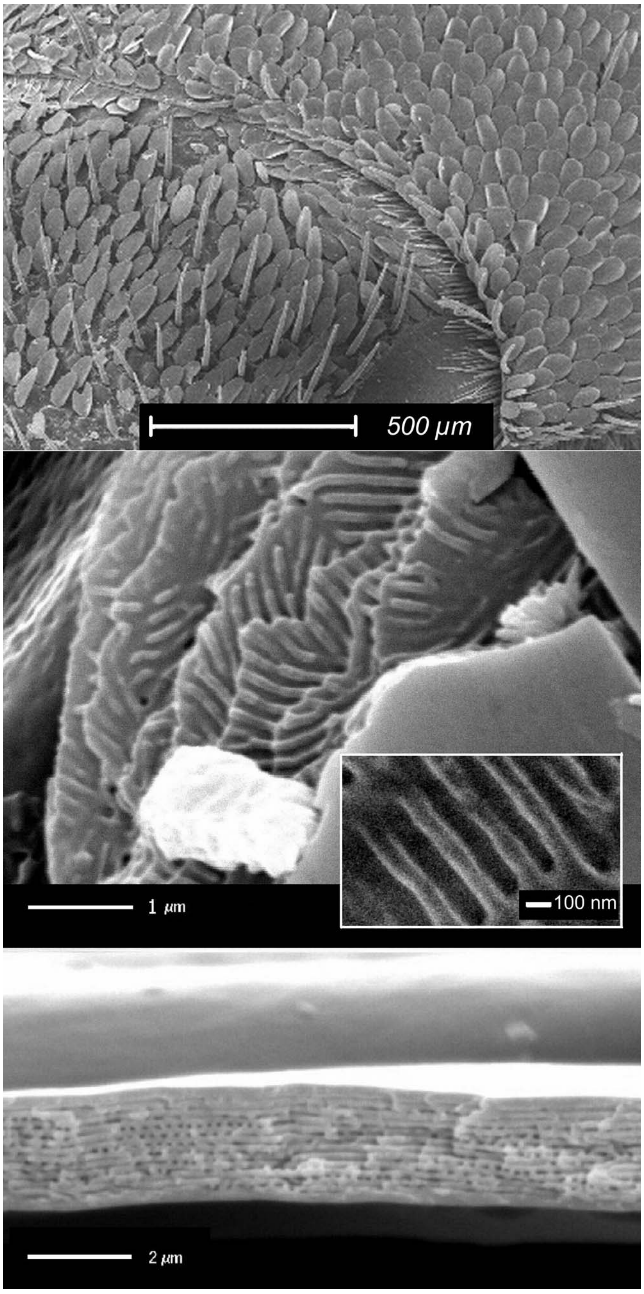

FIG. 4. Upper part: the scales on the dorsal side of the cuticle of the male *Hoplia coerulea*. The lower part shows the layered ultrastructure of a vertically broken scale and the middle part is a top view, showing the rods arrangement, on one of the layers.

$$(d+h)\bar{\varepsilon} = d\varepsilon_c + h\varepsilon \tag{3}$$

gives $\bar{\varepsilon}=1.81549$, leading to a global average refractive index $\bar{n}=1.34$. For an incidence $\theta=15°$, the first gap $(m=1)$ of a periodic multilayer with period $a=175$ nm and an average refractive index $\bar{n}=1.34$ is given by [14]:

$$\lambda = \frac{2a\sqrt{\bar{n}^2 - \sin^2\theta}}{m} \tag{4}$$

leading to an estimated dominant wavelength $\lambda=462$ nm. This describes well the "purplish blue" color [7,8] of the dry animal (450 nm for the experimental finding: 3% discrepancy).

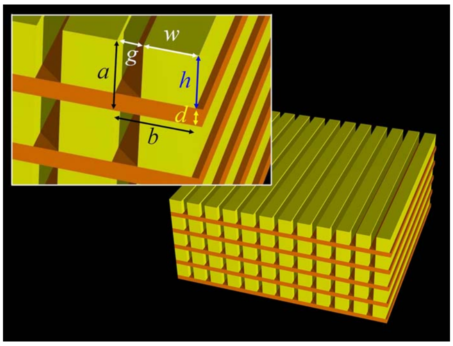

FIG. 5. (Color online) Model for the ultrastructure in the scales of the male *Hoplia coerulea*. The idealized structure is a stack of repeated corrugated layers (a two-dimensional photonic crystal). Each layer is composed of a basal slab supporting parallel rods with a rectangular section. The inset defines the typical dimensions, as measured from SEM. In the model presented in the present paper, $a=175$ nm, $h=140$ nm, $d=35$ nm, $b=175$ nm, $g=85$ nm, and $w=90$ nm. The refractive index of the basal slab and the rods is 1.6 (chitin). When air is replaced by water, in the voids of the structure, the refractive index changes from 1.00 to 1.33.

IV. MODEL FOR THE HYGROCHROMIC BEHAVIOR

When saturated with water, the structure changes color to become green. It can be assumed that water remains liquid and infiltrates into the structure to fill the voids. The air refractive index of the voids between the rods is then replaced by the refractive index of water, that is, with a dielectric function $\varepsilon_v=(1.33)^2=1.7689$.

We can repeat the calculation described above, adapting the voids refractive index. In the case of complete saturation with water, we find $\varepsilon_{\parallel}=2.17575$ and $\varepsilon_{\perp}=2.10315$, leading to an average response function of $\varepsilon=2.13945$ for the rods layer. Then, the whole structure increases its dielectric constant to $\bar{\varepsilon}=2.22$ and its global average refractive index to $\bar{n}=1.49$. At 15° of incidence, this change in refractive index produces a shift of the reflection peak to a dominant wavelength $\lambda=513$ nm [Eq. (4)].

Compared to the experimental value (530 nm), this result is only 3% off expectations, the same order of magnitude as for the dry state. This result is satisfactory, though if we look at the shift of wavelengths from dry to wet, the discrepancies add up rather than substract (discrepancy is positive for dry state and negative for wet state), so that the error affecting the shift is significantly higher. We cannot rule out the possibility that the whole structure in the scale experiences swelling, leading to a slight increase of the period a under water infiltration. The examination of the scales of the insect with the scanning electron microscopy (SEM) could never show any aperture by which liquid water could infiltrate the structure, so that it must be assumed that the material building the scales, including the structure inside, is permeable and that water infiltrates the structure by diffusing through the scale cortex. The rather large amount of time needed for this infiltration, in both directions (inbound and outbound) is compatible with this assumption. At least one form of chitin has been shown to swell under water absorption [15]. Swelling is a simple way of producing hygroscopic changes of color with multilayers. This effect was, for instance, recently demonstrated in artificial structures with chemically developed block-copolymer gels [16].

V. WETTING DYNAMICS

An important conclusion which results from the observations reported here is that the scales of the insect are hydrophilic. This is somewhat surprising as, in many cases, insects develop an hydrophobic surface, so that water does not stay too long on the cuticle. In the case of Lepidopters, butterflies, and moths, this is critical because water staying on the wings might results in a very inefficient flight. In these cases, the corrugation of the wing surface, with scales and structures on each scale, leads to superhydrophobicity, nonadhesion of water droplets and self-cleaning behavior. Other insects, however, can control the hydrophobic/hydrophillic behavior of their cuticle in a rather sophisticated way. Parker [17] describes the case of a Coleopter in the Namibia desert (in the genus *Stenocara*) where the cuticle has developed stripes of hydrophobic surfaces separated by hydrophillic areas which specifically help collecting water in low hygroscopic environments. The wettability of the insect cuticle is a trait that is then possibly controlled by evolution in both hydrophobic and hydrophillic cases. The cuticle of the *Dynastes hercules* and other related species, such as *Dynastes granti*, is clearly hydrophillic, as its change of color is also explained by water absorption in the voids left in the external part of the cuticle [5].

The change in coloration of *Hoplia coerulea* is clearly reversible, as several cycles of wetting/drying of our samples has confirmed. The way the changes occur, and in particular, the propagation of the dry (blue) state of the cuticle upon drying is also interesting. As Fig. 2 shows, the drying occurs by patches, rather than by a uniform change of color on the whole wet cuticle. This means that the scales are not drying individually, but rather collectively, forming domains of wet and complementary domains of dry groups of scales. The collective evacuation of water suggests that the internal structure of a scale can remain wet only if the exterior of the scale is surrounded with water, otherwise the porous structure evacuates itself rapidly. In the wet state, bridges of water connect a scale to its neighbors and these bridges are in equilibrium with the water infiltrated in the scales. In this way, the wetting of a given scale is favored by the presence of the bridges and then by the presence of water-filled scales in the immediate neighborhood. The situation bears resemblance to that found in a two-dimensional Ising model at low temperature [18], where the two "spin" states should be replaced by the dry and wet states of the scales. At low water contents (dry pseudo-"magnetization") the wet scales tend to form domains with minimal border lengths, as observed on Fig. 2, and predicted by an Ising model with low entropy. The porosity of chitinous material can be quite large: U.S. Patent 4575519 reports the use of artificial chitin with more than 90% porosity (see also Ref. [19]).

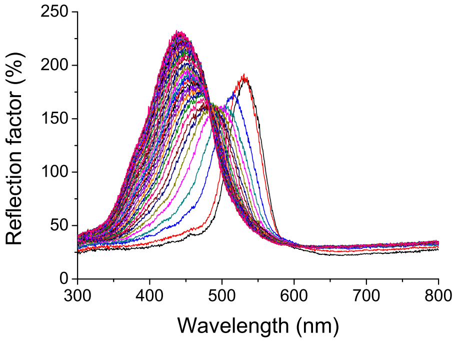

FIG. 6. (Color online) A large set of measurements showing the evolution of a piece of cuticle (of the order of 1 mm of diameter) switching from "green" to "blue" state, as the water evaporates.

The statistical mechanics Ising model has however a limitation, which is not apparent in the patterns shown in Fig. 2. The limitation lies in the fact that the boundary between a green and a blue domain is not sharp and shows an evolution in the reflected color. This evolution can be monitored by recording the color of a small surface of cuticle as the interface between the green and blue domains crosses the probed area as the sample dries. The result is shown in Fig. 6. If the domain boundary was much narrower than the probed surface diameter, the result of this measurement would distinctly show two peaks (one green and one blue) simultaneously, with amplitudes proportional to the area probed on each of the domains. Upon drying, the amplitude of the green peak would be transferred to the blue peak as the boundary progresses through the probed surface. This is not the case: Fig. 6, on the contrary, shows a single peak changing its spectral location from a green to a blue wavelength, indicating a continuous change of hygrometry saturation as the drying transformation progresses.

VI. CONCLUSION

The scales of the beetle *Hoplia coerulea* contain a very interesting periodic photonic structure, composed of a solid slab and a porous layer made with parallel rectangular rods. This group of layers is repeated a dozen times in the structure's thickness. The voids between the rods play an interesting role: the distance between two consecutive rods (or voids) is too small ($b=175$ nm) to produce diffraction for visible light, so that the layer appears as an effective medium of reduced refractive index, mixing air, and chitin. This provides the refractive index contrast to turn the structure into a color-selective Bragg mirror. The average refractive index of the whole structure and its vertical period explains reasonably well the blue coloration of the insect, both in the living state and dead, when dry in museums drawers.

At the contact of water, dead insects turn green and, to a large extent, this phenomenon is explained by the complete filling of the voids in the structure by liquid water. This phenomenon is observed when the insect's surface is contacted with liquid water, exposed to steam from boiling water or inserted in moist granular materials including humus from moist ground.

A material which change color at the contact of water can have important applications. Mimicking the vocabulary which calls "electrochrome" a material which changes its optical properties with the application of an external electric voltage and "thermochrome" a material which changes color with the change of temperature, the material encountered here can be called "hygrochrome." This class of material already exists, under certain artificial forms. For instance, a cloth formed by two layers is now currently manufactured: in this device, a back substrate, opaque, and colored, is covered by a porous layer that strongly diffuses light, so that the primary dry aspect of the surface is white. As water is applied to fill in the pores, the refractive index contrast with air is cancelled and the cover layer becomes translucent enough to leave a view on the substrate color (U.S. Patent 6953345). This cloth is commercialized as a toy for very young children, who can express their drawing skills with just innocuous clean water. The elimination of diffuse scattering by humidity condensation has been observed in the living world: the desert beetle *Cryptoglossa verrucosa* exhibits distinct color phases that range from light blue to jet black when subjected to extremes of low and high humidity, respectively [20].

Other systems, using light interferences in thin films, have also been described (see, for instance Ref. [21]). In spaces for exhibition or storage of humidity-sensitive items, a surface that translates humidity variations into spectacular color changes may be an extremely valuable passive warning device. Many other uses could be developed for the handling of goods (such as food) that should keep or avoid humidity.

Hygrochromic materials have been found on other living organisms: we already mentioned the *Dynastes hercules* and the color-changing tortoise beetles *Charidotella*, but the structure in *Hoplia coerulea* has also been observed in insects like longhorns. It can be expected that many other examples of natural humidity-sensitive materials will be found, while investigating physical visual effects on insects and other animals.

ACKNOWLEDGMENTS

The authors acknowledge the use of Namur Interuniversity Scientific Computing Facility (Namur-ISCF). M.R. was supported by the Belgian Fund for Scientific Research (F.R.S.-FNRS). One of us (J.P.V.) acknowledges the hospitality of Yvan and Françoise Diverchy in the village of Meyras, France, in the early stage of this work.

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