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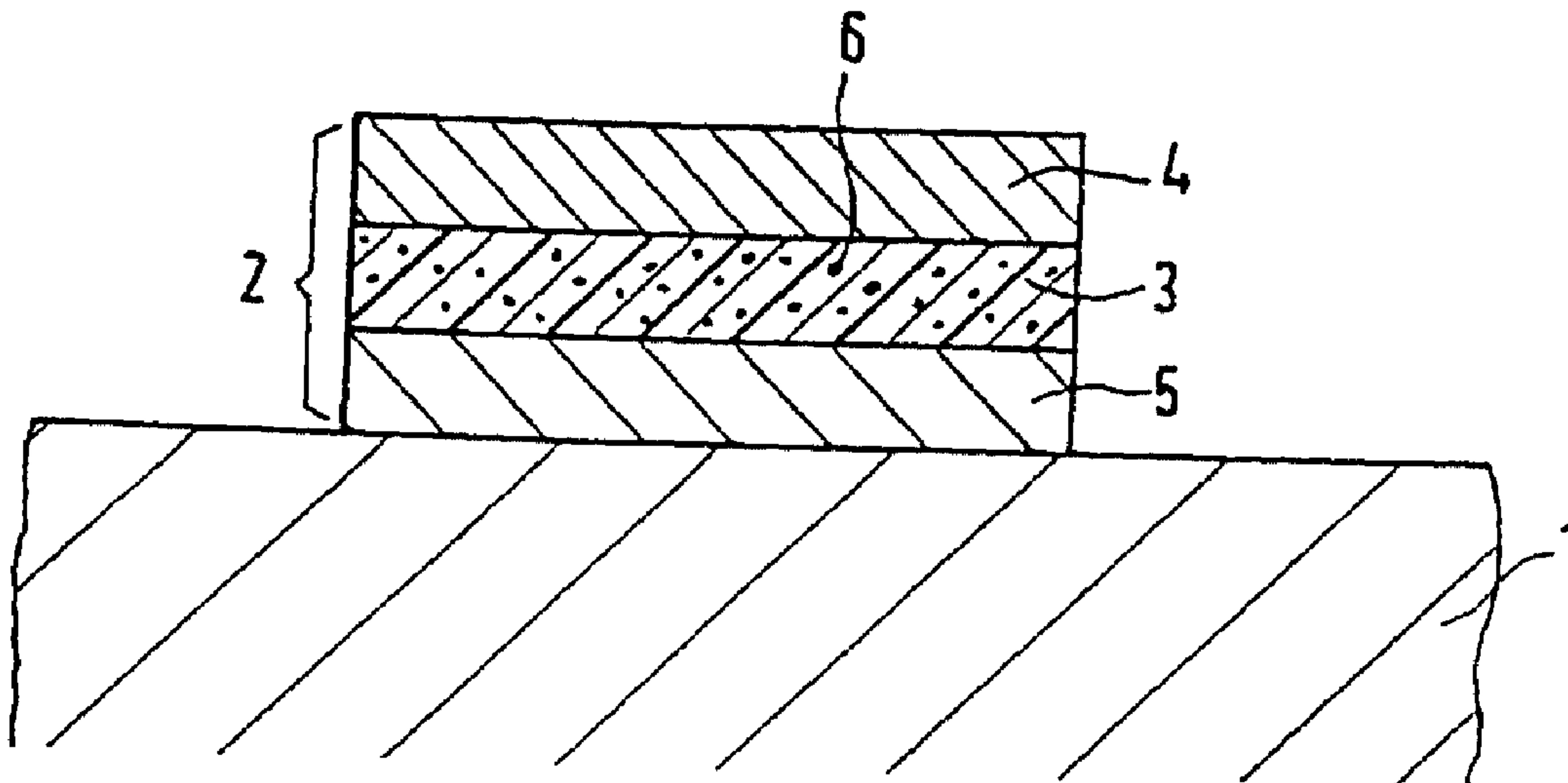
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(54) Title: DOCUMENT OF VALUE



(57) Abrégé/Abstract:

The invention relates to a printed document of value having at least one authenticity feature in the form of a luminescent substance based on doped host lattices. The host lattice has a strong crystal field and is doped with at least one chromophore with the electron configuration  $(3d)^2$ .

### Abstract

The invention relates to a printed document of value having at least one authenticity feature in the form of a luminescent substance based on doped host lattices. The  
5 host lattice has a strong crystal field and is doped with at least one chromophore with the electron configuration  $(3d)^2$ .

Document of value

This invention relates to a printed document of value having at least one authenticity feature in the form of a luminescent substance based on host lattices doped with chromophores with the electron configuration  $(3d)^2$ .

5 The term "document of value" refers according to the invention to bank notes, checks, shares, tokens, ID cards, credit cards, passports and other documents as well as labels, seals, packages or other elements for product protection.

Protecting documents of value against forgery by means of luminescent substances has been known for some time. The use of rare earth metals has also been discussed in this context. They have the advantage of having narrow-band characteristic  
10 spectral lines that facilitate reliable detection and delimitation over other spectra. The substances preferably used have either absorption or emission outside the visible spectral region.

If the emissions are at wavelengths between about 400 nanometers and about 700 nanometers, the luminescent substances are detectable with the eye upon suitable  
15 excitation. This is desirable for some applications, e.g. for an authenticity check by illumination with UV light. For other applications, however, it is of advantage if the emission is outside the visible spectral region since special detectors are then necessary for detecting the substances.

Luminophores with characteristic properties that are suitable for protecting  
20 documents of value and in particular for automatic authenticity detection are limited in number, however. Most inorganic and organic luminophores have uncharacteristic, broad spectra and are moreover often commercially available. This impedes their identification and makes it impracticable to use several of said substances simultaneously.

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Starting out from this prior art, the invention is based on the problem of increasing the number of luminophores suitable as an authenticity marking for documents of value and in particular providing documents of value with authenticity features in the form of luminescent substances that differ from documents of value with  
5 hitherto known luminophores by a characteristically altered excitation and/or emission spectrum.

The invention thus provides according to an aspect, for a document of value having at least one authenticity feature in the form of a luminescent substance based on doped host lattices. The document is characterized in that the host lattice is doped  
10 with at least one chromophore with the electron configuration  $(3d)^2$ .

The invention also provides according to another aspect, for a security element having a carrier material and at least one luminescent substance based on doped host lattices. The security element is characterized in that the host lattice is doped with at least one chromophore with the electron configuration  $(3d)^2$ .

15 The invention is based on the finding that the difficult detectability of certain luminescences with increasing emission wavelength in the IR spectral region can be utilized very advantageously to increase the protection from forgery.

According to the invention, documents of value are protected using at least one luminescent substance whose emission spectrum is outside the visible spectral re-  
20 gion, preferably even outside the responsiveness of silicon detectors.

The substances suitable for the inventive authenticity protection are luminescent substances based on host lattices doped with chromophores with the electron configuration  $(3d)^2$ . These may be chromophores of one kind or a mixture of at least two different chromophores. The inventive chromophores are preferably the transition metals titanium in oxidation state  $Ti^{2+}$ , hereinafter Ti(II), vanadium in oxidation state  $V^{3+}$ , hereinafter V(III), chromium in oxidation state  $Cr^{4+}$ , hereinafter Cr(IV),  
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manganese in oxidation state  $\text{Mn}^{5+}$ , hereinafter Mn(V), and iron in oxidation state  $\text{Fe}^{6+}$ , hereinafter Fe(VI).

The host lattices are inorganic matrices or organic chelates, e.g. apatites, spodosites, palmierites, forsterite, brushites, dahllites, ellestadites, francolites, monetites,  
5 morinites, whitlockites, wilkeites, voelckerites, pyromorphites, garnets, perovskites,

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olivines and certain silicates, titanates, vanadates, phosphates, sulfates, aluminates, zirconates.

Preferably, the host lattice is a compound with the formula:



5 where

$$a + b + c + d + e = 5;$$

$$f + g + h + j + k + l = 1;$$

$$m + n + p + q = 1;$$

$$x = 1 \text{ or } 2; \text{ and}$$

10 a, b, c, d, e each range from 0 to 5; and

f, g, h, j, k, l, m, n, p, q from 0 to 1.

A further preferred host lattice is a compound with the formula:



where  $a + b + c + d + e + f = 2$ ;

15  $g + h + j + k + l + m = 1$ ;

$n + p + q + r = 1$ ; and

a, b, c, d, e, f each range from 0 to 2; and

g, h, j, k, l, m, n, p, q, r from 0 to 1.

A further suitable host lattice is a compound with the formula:



where  $a + b + c + d + e + f = 2$ ;

$g + h + j = 1$ ; and

a, b, c, d, e, f each range from 0 to 2, and

g, h, j from 0 to 1.

25 In addition a host lattice with the formula:



is preferred, where  $a + b + c + d = 3$ ;

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$e + f + g = 1$ ; and

a, b, c, d each range from 0 to 3, and

e, f, g from 0 to 1.

Further, a particularly suitable host lattice has the formula:

5  $[Y_a La_b] [Si_c Ti_d] O_5$ ,

where  $a + b = 2$ ;

$c + d = 1$ ; and

a, b each range from 0 to 2, and

c, d from 0 to 1.

10 Preferably, the host lattice is further a compound with the formula:

$[Ba_a Ca_b Sr_c Pb_d Cd_e] (P_f V_g As_h Si_j S_k Cr_l O_4)_2$ ,

where  $a + b + c + d + e = 3$ ;

$f + g + h + j + k + l = 1$ ; and

a, b, c, d, e each range from 0 to 3, and

15 f, g, h, j, k, l from 0 to 1.

Also preferred is a host lattice with the formula:

$[Ba_a Ca_b Sr_c Pb_d Cd_e] (P_f V_g As_h Si_j S_k Cr_l O_4)_3 Cl$ ,

where  $a + b + c + d + e = 5$ ;

$f + g + h + j + l = 1$ ; and

20 a, b, c, d, e each range from 0 to 5, and

f, g, h, j, k, l from 0 to 1.

In addition, a particularly suitable host lattice has the formula:

$[Na_a K_b Rb_c Cs_d] [Se_e Se_f Cr_g Mo_h] O_4$ ,

where  $a + b + c + d = 2$ ;

25  $e + f + g + h = 1$ ; and

a, b, c, d each range from 0 to 2, and

e, f, g, h from 0 to 1.

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In addition, a particularly suitable host lattice has the formula:



where  $a + b + c + d = 1$ ; and

$e + f + g + h + i = 1$ , and

5  $a, b, c, d$  each range from 0 to 1, and

$e, f, g, h, i$  from 0 to 1. The host lattice  $\text{Ba SO}_4$  is especially preferred.

A further preferred host lattice is a compound with the formula:



where  $a + b + c + d + e + f + g + h + j + k + l + m + n + p + q + r + s = 1$ ;

10  $u + v + x = 1$ ; and

$a, b, c, d, e, f, g, h, j, k, l, m, n, p, q, r, s, u, v, x$  each range from 0 to 1.

In addition a host lattice with the formula:



is preferred, where  $a + b + c + d + e = 3$ ;

15  $f + g + h = 5$ ; and

$a, b, c, d, e$  each range from 0 to 3, and

$f, g, h$  from 0 to 5.

A further preferred host lattice is a compound with the formula:



20 where  $a + b + c + d = 1$ ;

$e + f + g + h = 2$ ; and

$a, b, c, d$  each range from 0 to 1, and

$e, f, g, h$  from 0 to 2

or a compound with the formula

25  $[\text{Mg}_a \text{Ca}_b \text{Sr}_c \text{Ba}_d] [\text{Al}_e \text{Cr}_f \text{Fe}_g \text{Ga}_h] \text{O}_7,$

where  $a + b + c + d = 1$ ;

$e + f + g + h = 4$ ; and

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a, b, c, d each range from 0 to 1, and  
e, f, g, h from 0 to 4.

Also preferred is a host lattice with the formula  
 $Y_2[Si_a Ti_b Zr_c] O_7$  or  $MgCa_2[Si_a Ti_b Zr_c] O_7$ ,

5 where  $a + b + c = 2$ , and  
a, b and c each range from 0 to 2.

A further suitable host lattice is a compound with the formula  
 $[Ba_a Ca_b Sr_c] [Si_d Ti_e Zr_f] O_5$ ,  
where  $a + b + c = 3$ ;

10  $d + e + f = 1$ ; and  
a, b, c each range from 0 to 3 and  
d, e, f from 0 to 1.

Further, a host lattice with the formula  
 $[Y_a La_b Zr_c] [P_d Si_e] O_4$  is preferred,

15 where  $a + b + c = 1$ ;  
 $d + e = 1$ , and  
a, b, c each range from 0 to 1,  
d, e from 0 to 1.

$Y PO_4$ ,  $La PO_4$ ,  $Zr Si O_4$  is especially preferred.

20 Further, a host lattice with the formula

$K [Ti_{2a} Zr_{2b}] (P O_4)_3$  is preferred,

where  $a + b = 1$ , and

a, b each range from 0 to 1.

$K Ti_2 (P O_4)_3$ ,  $K Zr_2 (P O_4)_3$  is especially preferred.

25 Host lattices with a strong crystal field are in particular preferred.

The positions and shapes of the excitation and/or emission bands are dependent on the insertion position of the chromophores in the host lattice. The chromophores can be present in the oxidic structural units of the host lattice both in the tetrahedral and in the octahedral configuration. However, the tetroxo configuration in the host  
5 lattice is preferred. In addition, the positions and shapes of the excitation and/or emission bands depend on the strength of the crystal field in the host lattice. The interactions occurring between chromophore and host lattice cause the electronic levels of the chromophores to change relative to their values and arrangement in the gas phase, i.e. to shift (in part mutually).

10 The concept of the crystal field will be explained by the example of the system  $\text{Cr}^{3+}$  in an octahedral environment [Imbusch, G.F.; Spectroscopy of Solid-State Laser-Type Materials, Ed: B. Di Bartolo; p 165; 1987]. Fig. 1a shows how the position and succession of the electronic levels of the chromophore  $\text{Cr}^{3+}$  depend on the strength of the crystal field, i.e. the interaction between chromophore and lattice (Tanabe-Sugano  
15 diagram). For weak octahedral crystal fields, the electronic state  ${}^4\text{T}_2$  is the first excited state above the ground state  ${}^4\text{A}_2$ , a broad-band luminescence from level  ${}^4\text{T}_2$  is observed. For strong crystal fields, finally, the state  ${}^2\text{E}$  weakly dependent on the crystal field is the first excited electronic state and a narrow-band emission from this level is observed. Analogous energy diagrams can be formulated for the inventive  $(3\text{d})^2$  con-  
20 figuration with the corresponding designations of the levels. For the important octahedral ( $\text{O}_h$ ) and tetrahedral ( $\text{T}_d$ ) configuration the level sequence is shown in Fig. 1b.

For protecting documents of value both broad-band and narrow-band luminescence can be used, but for reasons of selectivity narrow-band luminescence is preferred. These are observed in particular from the chromophores  $\text{Mn(V)}$  and  $\text{Fe(VI)}$  in  
25 host lattices with a strong crystal field.

Narrow band emission is usually spoken of when the bands occurring in the emission spectrum show an average half-value width of less than 50 nanometers.

However, this does not mean that bands having a half-value width outside this range do not solve the inventive problem.

Varying and combining the inventive chromophores and varying the host lattices open up numerous possibilities for influencing the excitation and emission spectra of the inventive luminescent substances and thus producing a great number of security features. Not only the evaluation of the excitation and/or emission spectra can be used for differentiation but also the lifetime of luminescence. The evaluation can take account of not only the wavelengths of the excitation or emission lines but also their number and/or shape and/or intensities, so that any desired coding can be represented.

The number of distinguishable inventive substances can be further increased if mixed crystals of the host lattices are also permitted or the host lattices are varied with additional dopings. For example, apatites and spodiosites or garnets and perovskites in certain concentration ratios of the starting substances can form mixed crystals in which the lattices run into one another. Connected therewith the crystal field acting on the chromophore can be changed.

Likewise, it is possible to incorporate further chromophores into the host lattices in addition to the inventive chromophores by doping and thus obtain combined luminescence of both systems or an energy transfer between the systems and utilize it for identification. For example, rare earth ions that maintain their typical luminescence in the host lattice due to their shielded shells are suitable for this purpose. These are preferably neodymium (Nd), holmium (Ho), erbium (Er), thulium (Tm) or ytterbium (Yb) cations or mixtures thereof.

If the document of value is marked not with one but with several of the inventive luminescent substances, the number of distinguishable combinations can be increased further. If different mixture ratios are moreover distinguished, the number of combinations can be increased again. Marking can be effected either at different places on the document of value or at the same place. If the luminescent substance is applied or

incorporated at different places on the document of value, a spatial code, in the simplest case e.g. a bar code, can be produced in this way.

Further, the forgery-proofness of the document of value can be increased by linking the special chosen luminescent substance e.g. in a document of value with  
5 other information of the document of value so that a check by means of a suitable algorithm is possible. The document of value can of course have further additional authenticity features, such as classic fluorescence and/or magnetism, besides the inventive luminescent substance.

The luminescent substances can be incorporated into the document of value in a  
10 great variety of ways according to the invention. Thus, the luminescent substances can be incorporated into a printing ink for example. It is also possible to admix the luminescent substance to the paper pulp or plastic composition during production of a document of value based on paper or plastic. Likewise, the luminescent substances can be provided on or in a plastic carrier material, which can for example be again  
15 embedded at least partly into the paper pulp. The carrier material, which is based on a suitable polymer, such as PMMA, and into which the inventive luminescent substance is embedded, can have the form of a security thread, a mottling fiber or a planchet. Likewise, for product protection the luminescent substance can be incorporated e.g. directly into the material of the object to be protected, e.g. into housings and plastic  
20 bottles.

However, the plastic or paper carrier material can also be fastened to any other object, e.g. for product protection. The carrier material is in this case preferably designed in the form of a label. If the carrier material is part of the product to be protected, as is the case e.g. with tear threads, any other design is of course also possible.  
25 It can be expedient in certain cases of application to provide the luminescent substance on the document of value as an invisible coating. It can be present all over or else in the form of certain patterns, such as stripes, lines, circles or in the form of al-

phanumeric characters. To guarantee the invisibility of the luminescent substance, either a colorless luminescent substance must, according to the invention, be used in the printing ink or coating lacquer or a colored luminescent substance used in such low concentration that the transparency of the coating is just given. Alternatively or  
5 additionally, the carrier material can be already colored suitably so that colored luminescent substances are not perceived due to their inherent color.

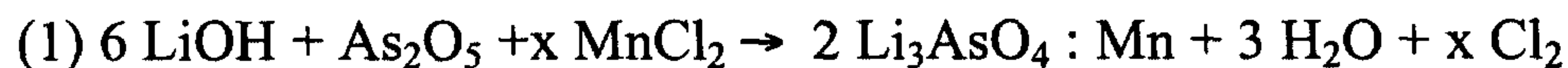
Usually, the inventive luminescent substances are processed in the form of pigments. For better processing or to increase their stability, the pigments can be present in particular as individually encapsulated pigment particles or be covered with an in-  
10 organic or organic coating. For example, the individual pigment particles are surrounded with a silicate sheath and can thus be more easily dispersed in media. Likewise, different pigment particles of a combination can be encapsulated jointly, e.g. in fibers, threads, silicate sheaths. Thus, it is e.g. no longer possible to change the "code" of the combination subsequently. "Encapsulation" refers here to complete encasing of  
15 the pigment particles, while "coating" includes partial encasing or covering of the pigment particles.

Hereinafter, some examples of the inventive luminescent substance will be explained in more detail.

#### Example 1

20 For the preparation the starting substances in oxidic form or substances that can be converted into oxides are mixed in a suitable ratio, e.g. as in equation (1), provided with the chromophore and then annealed, crushed, washed (e.g. with water), dried and ground. The chromophores used can be e.g.  $\text{Mn}_2\text{O}_3$ ,  $\text{MnO}$ ,  $\text{MnO}_2$ ,  $\text{MnCO}_3$ ,  $\text{MnCl}_2$ ,  $\text{KMnO}_4$  and organic manganese compounds. Their weight fraction based on the total  
25 mixture can be up to 20 percent by weight. Annealing is effected in the temperature range from 200 to 1700°C and a holding time of 0.2 to 24 hours, but preferably at 300 to 500°C and a holding time from 0.5 to 2 hours.

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To shift equilibrium in the direction of product formation, the preparation can additionally be mixed with  $\text{LiCO}_3$ , preferably 1 to 5 percent, and additional  $\text{LiOH}$ , preferably 1 to 20 percent by weight.

## 5 Example 2

Suitable quantities of sulfates (e.g.  $\text{K}_2\text{SO}_4$ ) or chromates (e.g.  $\text{K}_2\text{CrO}_4$ ) and the quantity of dopant, e.g.  $\text{Na}_2\text{FeO}_4$ , are dissolved in an alkaline medium. The doping with  $\text{Na}_2\text{FeO}_4$  can be up to 20 percent. Vaporization of the solvent yields the product, which is ground for further use.

10 Alternatively, a solid-state reaction can also be performed. For this purpose,  $\text{K}_2\text{SO}_4$  is ground with  $\text{NaCl}$  and intimately mixed with  $\text{Fe}_3\text{O}_4$ . The mixture is then annealed at temperatures between 700 and 1800°C. The product is ground for further use.

## Example 3

15 The method described in Example 2 can be altered so that a spray dryer is used for vaporizing the solvent. Further, the alkaline medium can consist completely or partly e.g. of a silicate suspension (e.g. LUDOX® AS-40, Dupont). In this case a material encased with silicate is obtained upon spray drying. A subsequent annealing process, preferably at temperatures from 200°C to 600°C, produces a  $\text{SiO}_2$  protective  
 20 layer and stabilizes the substance with respect to solubility in water. Additionally the material can be embedded into a polymer, e.g. PMMA, and processed into foil material. This is then cut into planchets.

Further embodiments and advantages of the invention will be explained hereinafter with reference to Figure 2.

25 Fig. 2 shows an inventive security element in cross section.

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Fig. 2 shows an embodiment of the inventive security element. The security element consists in this case of label 2 composed of paper or plastic layer 3, transparent cover layer 4 and adhesive layer 5. Label 2 is connected via adhesive layer 5 with any desired substrate 1. Substrate 1 may be a document of value, ID card, passport, certificate or the like, or another object to be protected, for example CD, package or the like. Luminescent substance 6 is contained within the volume of layer 3 in this example.

Alternatively, the luminescent substance might also be contained in a printing ink (not shown) that is printed on one of the label layers, preferably on the surface of layer 3.

Instead of providing the luminescent substance in or on a carrier material that is then fastened to an object as a security element, it is also possible according to the invention to provide the luminescent substance directly in the document of value to be protected or on the surface thereof in the form of a coating.

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Claims

1. A document of value having at least one authenticity feature in the form of a luminescent substance based on doped host lattices, characterized in that the host lattice is doped with at least one chromophore with the electron configuration  $(3d)^2$ .

2. A document of value according to claim 1, wherein the host lattice has a strong crystal field.

3. A document of value according to claim 1 or 2, wherein the chromophore is titanium in oxidation state 2 or vanadium in oxidation state 3 or chromium in oxidation state 4 or manganese in oxidation state 5 or iron in oxidation state 6.

4. A document of value according to any one of claims 1 to 3, wherein the document of value consists of paper or plastic.

5. A document of value according to any one of claims 1 to 4, wherein the authenticity feature is incorporated into the volume of the document of value or present in a layer applied to the document of value.

6. A document of value according to any one of claims 1 to 5, wherein the luminescent substance is provided on the document of value as an invisible, at least partial coating.

7. A document of value according to any one of claims 1 to 6, wherein the luminescent substance is admixed to a printing ink.

8. A document of value according to any one of claims 1 to 7, wherein the coating has the form of one or more stripes.

9. A document of value according to any one of claims 1 to 8, wherein the host lattice is additionally codoped with at least one representative from the group of rare earth metal cations.

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10. A document of value according to claim 9, wherein the rare earth metal cation is selected from neodymium (Nd), holmium (Ho), erbium (Er), thulium (Tm) and ytterbium (Yb).

11. A document of value according to any one of claims 1 to 10, wherein the host lattice is selected from the class of apatites, spodiosites, palmierites, forsterites, brushites, dahllites, ellestadites, francolites, monetites, morinites, whitlockites, wilkeites, voelckerites, pyromorphites, garnets, perovskites, silicates, titanates, vanadates, and phosphates.

12. A document of value according to any one of claims 1 to 11, wherein the host lattice is a compound with the formula:



where

$$a + b + c + d + e = 5;$$

$$f + g + h + j + k + l = 1;$$

$$m + n + p + q = 1;$$

$$x = 1 \text{ or } 2; \text{ and}$$

a, b, c, d, e each range from 0 to 5; and

f, g, h, j, k, l, m, n, p, q from 0 to 1.

13. A document of value according to any one of claims 1 to 11, wherein the host lattice is a compound with the formula:



where  $a + b + c + d + e + f = 2$ ;

$$g + h + j + k + l + m = 1;$$

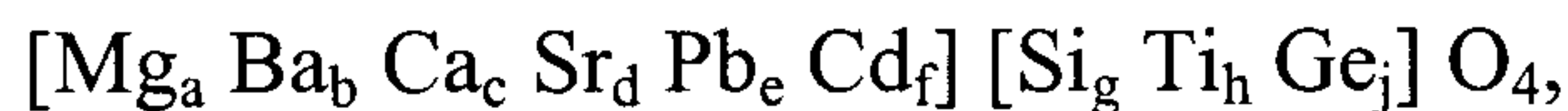
$$n + p + q + r = 1; \text{ and}$$

a, b, c, d, e, f each range from 0 to 2; and

g, h, j, k, l, m, n, p, q, r from 0 to 1.

14. A document of value according to any one of claims 1 to 11, wherein the host lattice is a compound with the formula:

- 15 -



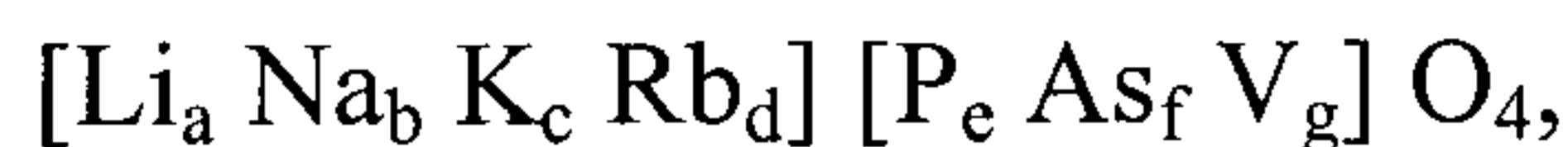
where  $a + b + c + d + e + f = 2$ ;

$g + h + j = 1$ ; and

$a, b, c, d, e, f$  each range from 0 to 2, and

$g, h, j$  from 0 to 1.

15. A document of value according to any one of claims 1 to 11, wherein the host lattice is a compound with the formula:



where  $a + b + c + d = 3$ ;

$e + f + g = 1$ ; and

$a, b, c, d$  each range from 0 to 3, and

$e, f, g$  from 0 to 1.

16. A document of value according to any one of claims 1 to 11, wherein the host lattice is a compound with the formula:



where  $a + b = 2$ ;

$c + d = 1$ ; and

$a, b$  each range from 0 to 2, and

$c, d$  from 0 to 1.

17. A document of value according to any one of claims 1 to 11, wherein the host lattice is a compound with the formula:



where  $a + b + c + d + e = 3$ ;

$f + g + h + j + k + l = 1$ ; and

$a, b, c, d, e$  each range from 0 to 3, and

$f, g, h, j, k, l$  from 0 to 1.

18. A document of value according to any one of claims 1 to 11, wherein the host lattice is a compound with the formula:

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where  $a + b + c + d + e = 5$ ;

$f + g + h + j + l = 1$ ; and

$a, b, c, d, e$  each range from 0 to 5, and

$f, g, h, j, k, l$  from 0 to 1.

19. A document of value according to any one of claims 1 to 11, wherein the host lattice is a compound with the formula:



where  $a + b + c + d = 2$ ;

$e + f + g + h = 1$ ; and

$a, b, c, d$  each range from 0 to 2, and

$e, f, g, h$  from 0 to 1.

20. A document of value according to any one of claims 1 to 11, wherein the host lattice is a compound with the formula:



where  $a + b + c + d = 1$ ; and

$e + f + g + h + i = 1$ , and

$a, b, c, d$  each range from 0 to 1, and

$e, f, g, h, i$  from 0 to 1.

21. A document of value according to any one of claims 1 to 11, wherein the host lattice is a compound with the formula:



where  $a + b + c + d + e + f + g + h + j + k + l + m + n + p + q + r + s = 1$ ;

$u + v + x = 1$ ; and

$a, b, c, d, e, f, g, h, j, k, l, m, n, p, q, r, s, u, v, x$  each range from 0 to 1.

22. A document of value according to any one of claims 1 to 11, wherein the host lattice is a compound with the formula:



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where  $a + b + c + d + e = 3$ ;

$f + g + h = 5$ ; and

$a, b, c, d, e$  each range from 0 to 3, and

$f, g, h$  from 0 to 5.

23. A document of value according to any one of claims 1 to 11, wherein the host lattice is a compound with the formula:



where  $a + b + c + d = 1$ ;

$e + f + g + h = 2$ ; and

$a, b, c, d$  each range from 0 to 1, and

$e, f, g, h$  from 0 to 2

or a compound with the formula



where  $a + b + c + d = 1$ ;

$e + f + g + h = 4$ ; and

$a, b, c, d$  each range from 0 to 1, and

$e, f, g, h$  from 0 to 4.

24. A document of value according to any one of claims 1 to 11, wherein the host lattice is a compound with the formula



where  $a + b + c = 2$ , and

$a, b$  and  $c$  each range from 0 to 2.

25. A document of value according to any one of claims 1 to 11, wherein the host lattice is a compound with the formula



where  $a + b + c = 3$ ;

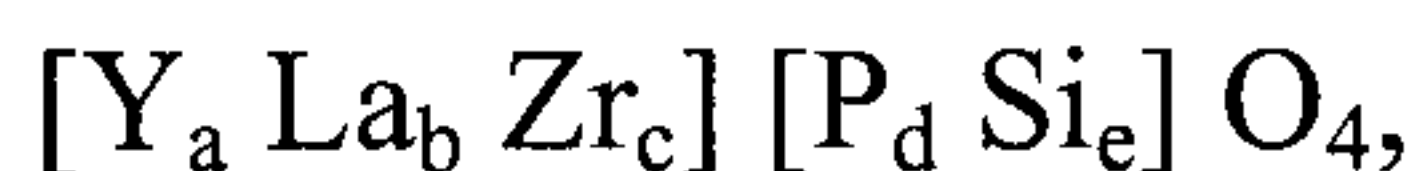
$d + e + f = 1$ ; and

$a, b, c$  each range from 0 to 3 and

$d, e, f$  from 0 to 1.

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26. A document of value according to any one of claims 1 to 11, wherein the host lattice is a compound with the formula



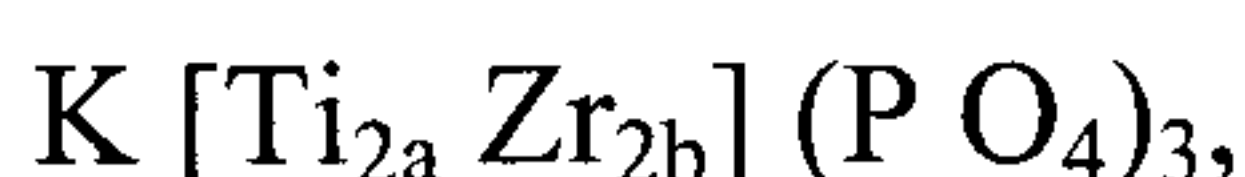
where  $a + b + c = 1$ ;

$d + e = 1$ , and

$a, b, c$  each range from 0 to 1,

$d, e$  from 0 to 1.

27. A document of value according to any one of claims 1 to 11, wherein the host lattice is a compound with the formula:



where  $a + b = 1$ , and

$a, b$  each range from 0 to 1.

28. A document of value according to any one of claims 1 to 27, wherein the chromophores are present in the host lattice in the tetroxo configuration.

29. A document of value according to any one of claims 1 to 28, wherein the luminescent substance is present as pigment particles.

30. A security element having a carrier material and at least one luminescent substance based on doped host lattices, characterized in that the host lattice is doped with at least one chromophore with the electron configuration  $(3d)^2$ .

31. A security element according to claim 30, wherein the host lattice has a strong crystal field.

32. A security element according to claim 30 or 31, wherein the security element has the form of a stripe or band.

33. A security element according to any one of claims 30 to 32, wherein the carrier material is formed as a security thread, planchet or mottling fiber.

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34. A security element according to any one of claims 30 to 33, characterized in that the security element is formed as a label.

35. A security element according to any one of claims 30 to 34, characterized in that the at least one luminescent substance is embedded in the carrier material or applied to the carrier material.

36. A method for producing a document of value as defined in any one of claims 1 to 29, the method comprising admixing the luminescent substance with a printing ink and printing the document.

37. A method for producing a document of value as defined in any one of claims 1 to 29, characterized in that the luminescent substance is applied by a coating process.

38. A method for producing a document of value as defined in any one of claims 1 to 29, characterized in that the luminescent substance is incorporated into the volume of the document of value.

39. A method for producing a document of value as defined in any one of claims 1 to 29, characterized in that the luminescent substance is supplied to the document of value by accordingly prepared mottling fibers.

40. A method for producing a document of value as defined in any one of claims 1 to 29, characterized in that the luminescent substance is supplied to the document of value by an accordingly prepared security thread.

41. A method for authenticity testing of a document of value as defined in any one of claims 1 to 29 or a security element as defined in any one of claims 30 to 35, the method comprising determining the wavelengths and/or number and/or shape and/or intensities of the emission lines and/or excitation bands of the luminescent substance.

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42. A method for authenticity testing of a document of value or security element according to claim 41, characterized in that the emission lines and/or excitation bands represent a coding.

43. A method for authenticity testing of a document of value according to any one of claims 1 to 29 or a security element according to any one of claims 30 to 35, the method comprising determining the lifetimes of luminescence of the luminescent substance.

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FIG. 1a

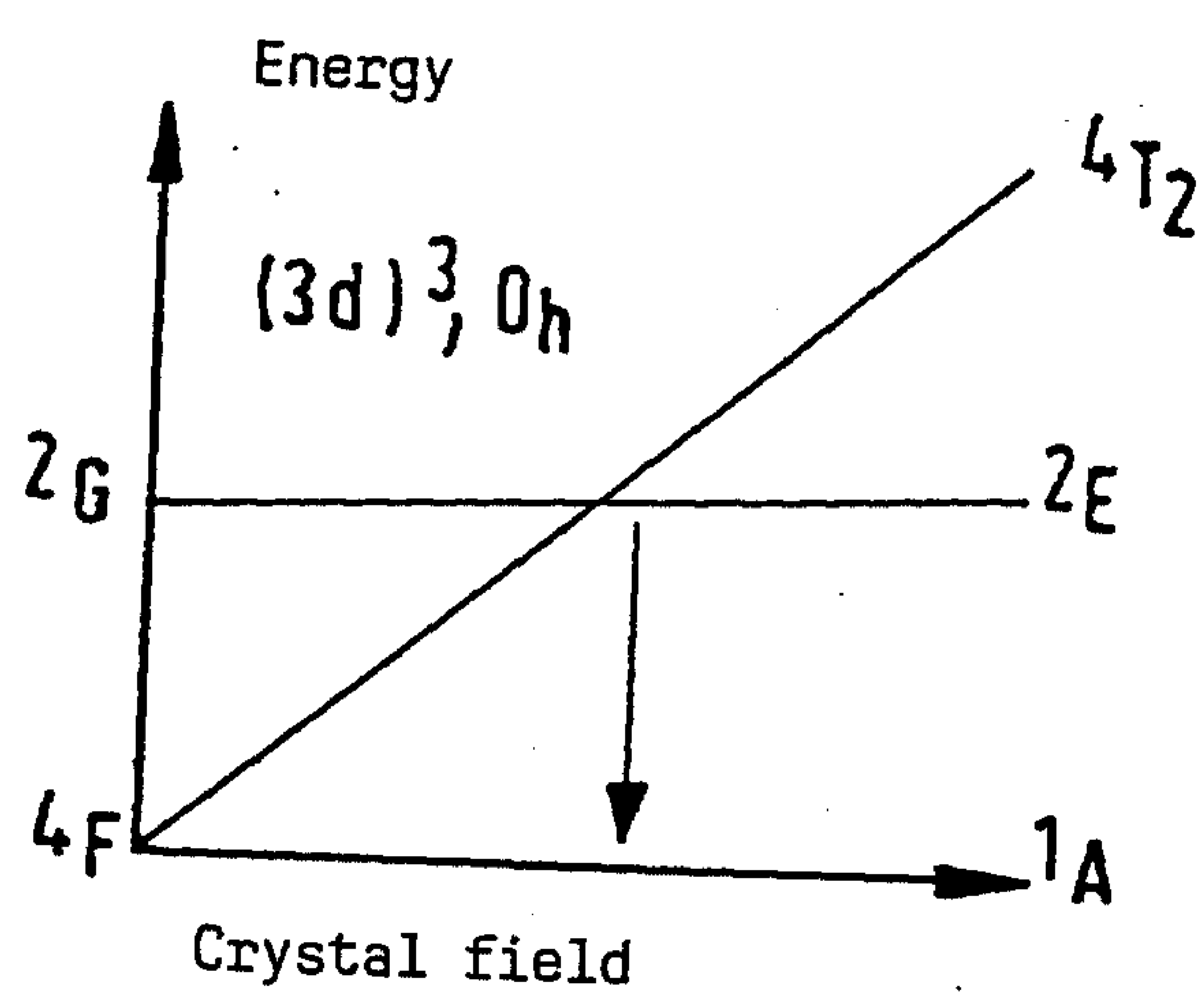


FIG. 1b

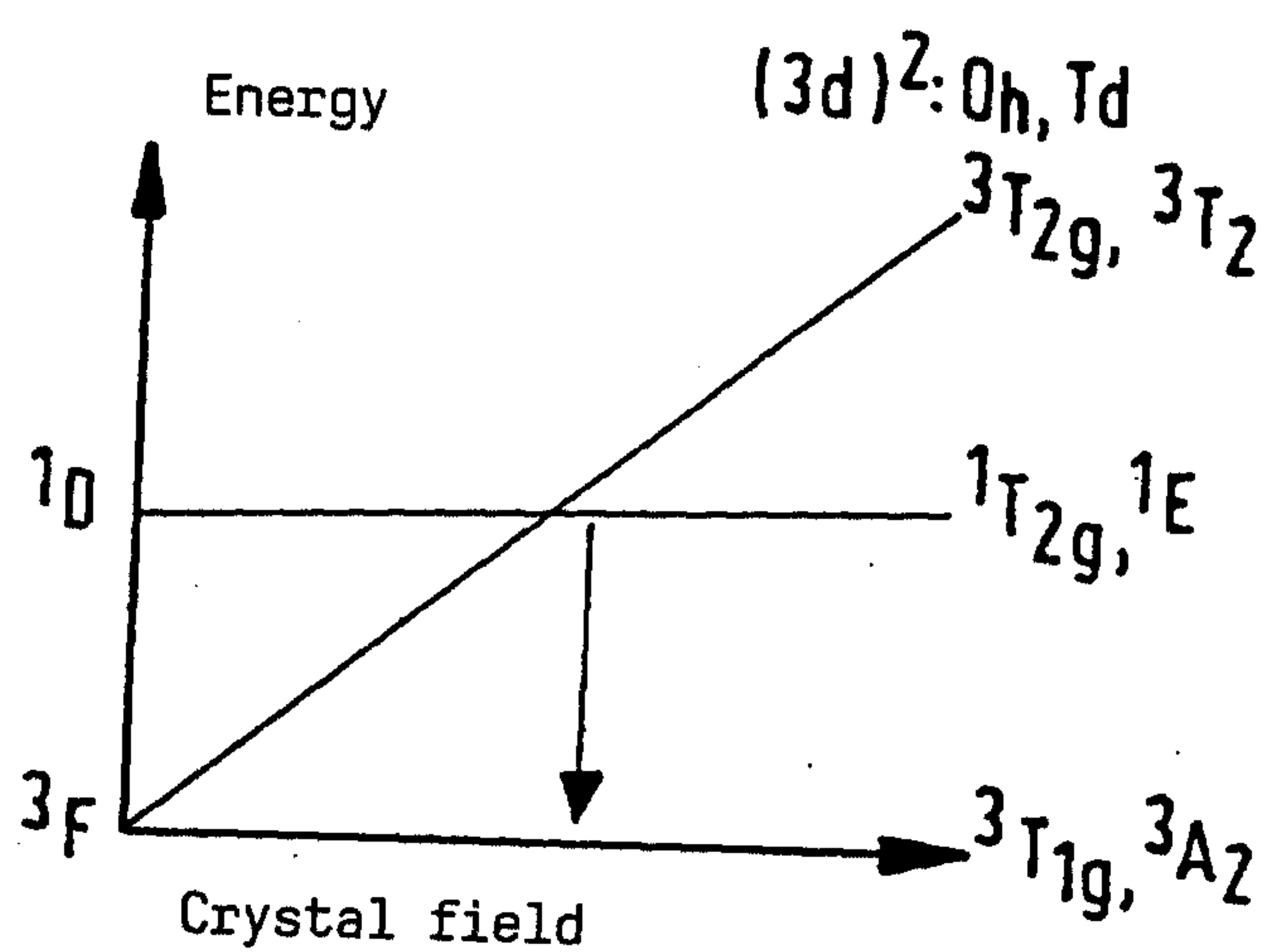


FIG. 2

