On the conductivity character of rare-earth compounds

Autor(en): **Hulliger, F.**

Objekttyp: **Article**

Zeitschrift: **Helvetica Physica Acta**

Band (Jahr): **41 (1968)**

Heft 6-7

PDF erstellt am: **22.07.2024**

Persistenter Link: https://doi.org/10.5169/seals-113952

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The conclusion is that under the actual conditions, direct radiative hole-electron recombination may successfully compete with the ordinary hole trapping process. More accurate tests of the validity of the suggested model should be possible from, for example, studies of photo-electromagnetic effect.

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On the Conductivity Character of Rare-Earth Compounds

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(1. V. 68)

Abstract. The conductivity type of the rare-earth compounds is correlated with the electronic configuration of the cations. Simple halides, chalcogenides, pnictides as well as dihydrides, dicarbides and hexaborides are briefly discussed.

My interest in rare-earth compounds derives from the search of ferromagnetic semiconductors which was proposed to me as early as 1955 by Prof. G. Busch. It is a great pleasure for me, therefore, to honour Prof. Busch on his 60th birthday by dedicating to him the present notes on rare-earth compounds, the physics of which has been elucidated considerably by his investigations.

With certain exceptions the rare-earth atoms Ln in chalcogenides, pnictides or even in intermetallic compounds behave like transition elements of the scandium group with additional f electrons in discrete levels. The exceptions reflect the small differences in the ionization energies of the f electrons of $4f^q$ cations. Because of the strong spin-orbit coupling and the small radius of the $4f$ electrons the crystal field is

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of minor influence and plays a role only at temperatures of the order of 10 °K. Therefore, the crystal structures of the Ln compounds are independent of the cation f configuration and are determined by the size of these cations only. Moreover, magnetic measurements afford an unambiguous determination of the number of valence electrons available for bonding.

In order to understand the metallic behaviour of certain Ln halides, chalcogenides and pnictides, it is helpful to remember that we are dealing with a special class of transition-element compounds. In the normal transition-element compounds 'unexpected' metallic properties are always due to delocalized d electrons, and the rare-earth compounds are no exception. The $4f$ electrons of the rare-earth ions, however, are never delocalized since they are so strongly attached by the core potential that small average distances from the nucleus result. On the other hand, the interelectronic repulsion between $4f$ electrons is so large as to cancel the attraction almost completely which leads to ionization energies comparable to those of valence electrons with far larger radii, such as the $5d$ electrons. This gives rise to a competition between the configurations $4f^{q-1}5d^1$ and $4f^q5d^0$ in Ln^0 or Ln^{2+}, particularly at the beginning of the half-periods (La, Ce ... and Gd, Tb ...) and hence to a low stability of the divalent state. A further consequence is the rapid increase of the $4f$ ionization energy as a function of the ionic charge. Therefore, $+ 3$ is the common valence state of the rare-earth ions, while a valency of $+ 4$ is possible only in certain favourable cases.

The electronic configurations of the gaseous rare-earth atoms are $5d^1\,6s^2$ for La, $4f^7\,5d^1\,6s^2$ for Gd, $4f^{14}\,5d^1\,6s^2$ for Lu and $4f^q\,6s^2$ for the remaining Ln atoms. Divalent states, therefore, might be possible for all rare-earth elements, though La, Gd and Lu are rather expected to form the typical trivalent rare-earth ions. Interactions in the crystalline compounds, however, modify the energy scale and smear out the finer details of the separate atoms. Nevertheless, the extraordinary case of a $4f^7\,5d^1$ configuration is realized in $CaF_2 : Gd^{2+}$ [1]. This, of course, is possible only in very diluted Ln^{2+} compounds. In undiluted La^{2+} and Gd^{2+} compounds, such as $Sr_{1-x}La_xS$, $Eu_{1-x}La_xS$, or $Ba_{1-x}Gd_xS$ for, say, $x > 0.1$, the discrete $5d$ levels broaden into an incompletely-filled conduction band. This is not surprising if we take into account that the d-electron levels in Sc, Y and La ... Lu are less stable than in the corresponding Group IV elements Ti, Zr and Hf, and that localized d^1 states are extremely rare even in Group IV compounds. Normally, excess d-electrons interact with neighbours so that formal d^1 configurations give rise to the formation of metallic d bands unless the degeneracy of the occupied d level is removed by the formation of separate cation pairs.

Such d-band conduction is also responsible for the metallic character of apparently divalent compounds of the other rare-earth atoms. Although in these elements the configurations $4f^{q-1}5d^1$ obviously have higher energies than the configuration $4f^q5d^0$, this difference is only small for the first elements of the two sequences. Since the last-added f electron is rather loosely bound, the crystal-field stabilization of certain d orbitals may be sufficient to invert the two energies in a crystalline compound. JØRGENSEN [2] has derived an expression for the energy of $4f^q \rightarrow 4f^{q-1}5d^1$ excitations in different environment:

$$W_2 + (q-1)\,(E-A)_2 + k_4\,D + k_5\,E^3 + k_6\,\zeta_{4f}\,.$$

Here, W_2 is a standard of reference for comparison within a given series where only q is varied. $(E\text{–}A)_2$ indicates that the gradually increasing stabilization of the $4f$-orbital energy is the result of a difference between the increase E of the core attraction and the increase A of the interelectronic repulsion in the $4f$ shell. The third term is due to the change with q of the spin-pairing energy [3]

$$D\,[\langle S\,(S+1)\rangle - S\,(S+1)] = D\left[\frac{3}{4}\,q - \frac{3\,q\,(q-1)}{16\,l+4} - S\,(S+1)\right].$$

The fourth term represents the contribution due to RACAH's extra-stabilization of H and I ground terms by amounts proportional to RACAH's parameter of interelectronic repulsion E^3. The last term accounts for the difference in spin-orbit coupling energy. E^3 and the LANDÉ parameter ζ_{4f} are known from internal $4f^q$ transitions or can be estimated from the data for trivalent ions. For Ln^{2+} the values are roughly 10% lower than those for Ln^{3+}. The coefficients k_i are [2, 3]

$$13\,k_4 = 8\,(q-1) \text{ for } q = 1 \ldots 7, \text{ and } 8\,(q-14) \text{ for } q = 8 \ldots 14\,,$$

$$k_5 = 0, +9, +12, 0, -12, -9, 0 \text{ for } q = 1, \ldots, 7 \text{ and } q = 8, \ldots, 14\,,$$

$$k_6 = +2, +1, +1/2, 0, -1/2, -1, -2 \text{ for } q = 1, \ldots, 7 \text{ respectively,}$$

$$\text{and} + 3/2, +1, +1/2, 0, -1/2, -1, -3/2 \text{ for } q = 8, \ldots, 14\,.$$

Values of the parameters for different environments are [3, 4] (all energies in kK = 10^3 cm^{-1})

Ln^{2+} in CaF_2:	$W_2 = -17$	$(E-A)_2 = 3.8$	$D = 5.2$
Ln^{3+} in CaF_2:	$+31$	5.0	6.2
LnS solid:	-25	3.0	(5.2)
Ln_2O_3 solid:	$+21$	3.8	5.2
gaseous Ln^{2+}:	-8	3.7	5.5
gaseous Ln^{3+}:	$+50$	4.0	(6.7)

Pr^{2+} $(q = 3)$:	$E^3 = 0.41$	$\zeta_{4f} = 0.65$
Sm^{2+} $(q = 6)$:	0.48	1.05
Tm^{2+} $(q = 13)$:	–	2.51

Energies calculated [4, 5] (and partly verified by optical measurements [1, 5]) for $f^q \rightarrow f^{q-1}d^1$ transitions of divalent and trivalent rare-earth ions in CaF_2 are shown in Figure 1. If the RACAH and spin-orbit corrections are neglected, then the energy differences fall on two straight lines making a jump of $\sim 8D$ at the half-filled shell. Curves for compounds with other anions are similar but less steep and shifted downwards for less electronegative anions. Figure 1 readily explains why no divalent La compounds are known, not even with such electronegative anions as fluorine. Stability calculations for the dichlorides [6] reveal that $LaCl_2$, $CeCl_2$, $GdCl_2$, and $TbCl_2$ will not occur as solids. The first dichloride in this sequence, that has been prepared, is $NdCl_2$ [7], which is an insulator containing the $4f^4$ ion Nd^{2+}. $SmCl_2$, $EuCl_2$, $DyCl_2$

[8], $TmCl_2$ and $YbCl_2$ [9, 10] are further examples of non-metallic Ln^{2+} compounds. Among the iodides LaI_2, CeI_2, PrI_2, NdI_2, SmI_2, EuI_2, GdI_2, TmI_2, and YbI_2 are known [10–12]. This is only an apparent contradiction to Figure 1. The diiodides of the elements with negative ionization energies are metallic and contain in fact the rare-earth ion in the trivalent state [11]. Moreover, the non-metallic, isomorphous [10] compounds NdI_2, SmI_2 and EuI_2 crystallize in a monoclinic structure [13] which is different from that of the metallic iodides (these latter may be of the CdI_2 type, since the metallic cations are smaller and comparable in size with Tm^{2+} and Yb^{2+}, the diiodides of which adopt this structure [9]).

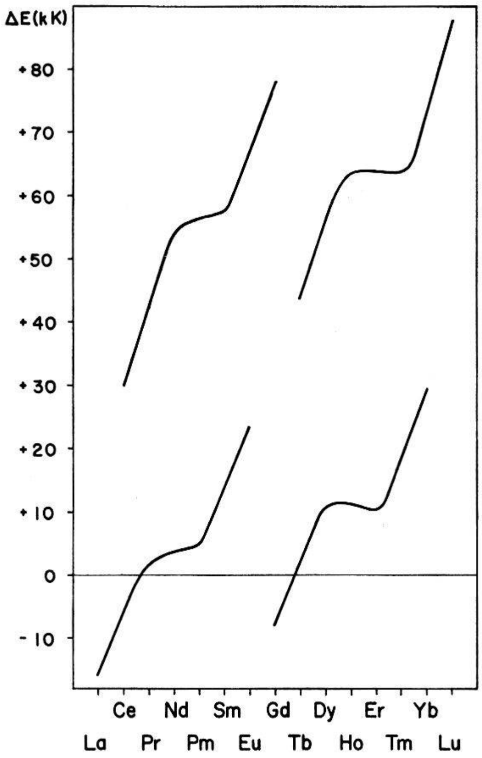

Figure 1

Energies for the $4f^q \rightarrow 4f^{q-1}5d^1$ excitation in divalent (lower curves) and trivalent (upper curves) rare-earth ions in CaF_2. $1\ kK = 10^3\ cm^{-1}$.

The rare-earth monochalcogenides, on the other hand, all crystallize in the same structure of the rocksalt type [14, 15]. Since the electronegativities of the anions are lower, whereas the Ln concentration and hence the cation-cation interactions are increased with respect to the halides, it is not surprising that only the rare-earth elements with the largest $f^q - f^{q-1}d^1$ separations [4], Sm, Eu, Yb and probably Tm in TmTe [15], form non-metallic compounds [16–19]. In the remaining monochalcogenides the least-bound Ln valence electron has become a metallic *d* electron [20–24]. The difference between the electronic configuration in metallic $Ln^{3+}X$ and in non-metallic $Ln^{2+}X$ clearly shows up in the curve of the lattice constants (Figure 2). The additional cation-cation bonds in $Ln^{3+}X$ reduce the effective diameter of the Ln ion by 0.3 to 0.4 Å. In SmTe and EuTe the electronic transition $f^q \rightarrow f^{q-1}$ 'd^1' can be made to take place at room temperature by application of pressure (~ 60 kbar [25]).

In NaCl-type Ln compounds the *d* band will be broadest with La and narrower with Lu. This correlates with the decreasing radius of the cations: the overlapping of the 5*d* functions decreases in the metallic LnX on going from LaX to LuX, therefore, the electrical conductivity must decrease as well. For the same reason *d*-band conductivity decreases in the sequence LnS → LnSe → LnTe. It is interesting to note that the metallic sulfides are stable in the rocksalt structure with sulfur deficiencies of up to 25% [26]. The concentration of conduction electrons in the *d* band thus increases from 1 to 1.5 per cation.

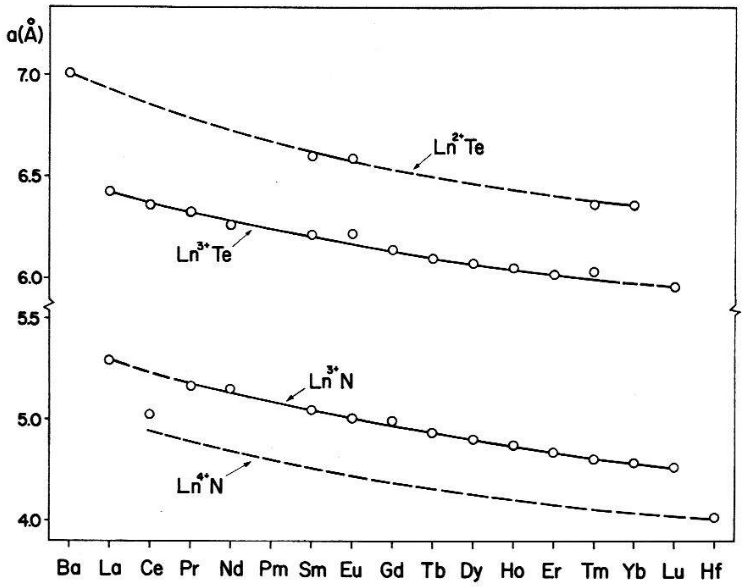

Figure 2

Influence of the cation valency on the lattice constants of rocksalt-type tellurides and nitrides.

In non-metallic monochalcogenides the effective activation energy [27] will depend not only upon the position of the bands due to the valence electrons (which would produce the usual decrease of ΔE in the sequence oxide → telluride) but also upon the relative positions of the *f* levels and the bottom of the $d\varepsilon$ band [28]. The latter goes to lower energies as the crystal-field splitting increases but also as the *d*-band width increases with enhanced cation-cation interaction resulting from shorter Ln–Ln distances.

It is noteworthy that no superconducting transition was found in YTe ($T_n = 1.02\,°K$) [29], LaS and LaSe ($T_n = 1.25\,°K$) [30]. The isoelectronic analogues of the superconductors ZrN ($T_c = 9\,°K$) and HfN ($T_c = 6.2\,°K$) [29] would be YO and LuO; therefore it is not excluded that YS and LuS are superconductors.

The marked difference between divalent and trivalent rare-earth radii provides a means of determining whether certain rare-earth compounds are semiconductors or metals. As a first example we plot in Figure 3 the lattice constants of the tetragonal CaC_2-type carbides versus the lattice constants of the cubic monosulfides (instead of using ill-defined ionic radii). As expected we obtain smooth curves if we choose the correct valency of the rare-earth cations. We thus conclude that EuC_2 and YbC_2 are non-metallic like CaC_2 whereas the remaining dicarbides contain trivalent cations and hence are metallic. Since the radius contraction due to the metallic *d–d* interactions in $Ln^{3+}S$ is slightly different from that in $Ln^{3+}C_2$, the scale of the Ln^{3+} radii is slightly wrong with respect to the scale of the Ln^{2+} radii and therefore the curves for the non-metallic compounds do not exactly coincide with those of the metallic compounds. We note that most dicarbides are antiferromagnetic [31] while the magnetic properties of EuC_2 are unknown. YC_2 is superconducting below 3.88 °K [32].

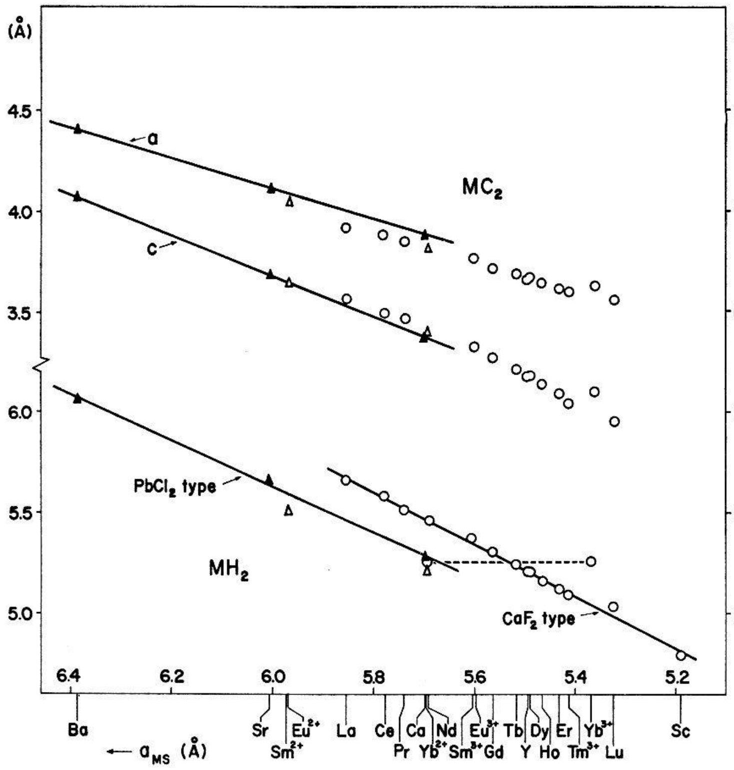

Figure 3

Lattice constants of the dicarbides (above) and dihydrides (below) of the rare-earth and alkaline-earth metals as functions of the cation radii (represented by the lattice constants of the monosulfides). For the orthorhombic dihydrides $(a\, b\, c)^{1/3}$ is plotted. Divalent cations are indicated as triangles (black in the case of the alkaline-earth compounds).

As a second example we consider the dihydrides. Here the different bonding character of the metallic and the semiconducting compounds is already evident from the occurrence of two different crystal structures, the cubic CaF_2 and the orthorhombic $PbCl_2$ types [14, 33, 34]. Diamagnetic YbH_2 [35] and ferromagnetic EuH_2 ($\theta_f = 25$ °K) [36–38] are the only possible non-metallic rare-earth dihydrides. With the exception of ferromagnetic NdH_2 ($\theta_f = 9.5$ °K), the cubic metallic hydrides are either antiferromagnetic or do not order magnetically [39, 40]. Concluding from the superconductive transition temperature of Cu-type lanthanum metal ($T_c \sim 6$ °K) a value $T_c \sim 0.25$ °K [41] is estimated for LaH_2; down to 0.33 °K it is normal [41]. YbH_2 exists also in a cubic high-temperature modification [35], which according to our plot contains half Yb^{3+} and Yb^{2+} and thus must be metallic. Of course, the size criterion is only useful if the non-metallic compounds require divalent cations.

Similar results are obtained for the hexaborides. The lattice constants of YbB_6 and EuB_6 (which is ferromagnetic below 8 °K [42]) fit the straight line defined by the alkaline-earth hexaborides, assuming divalent cations. YbB_6 and EuB_6 thus may be semiconductors as are CaB_6, SrB_6 and BaB_6 [43]. SmB_6 is seen to contain both Sm^{2+} and Sm^{3+} ions. At low temperatures it may consist of divalent ions only. In all the other hexaborides the rare-earth ions are trivalent. YB_6 and LaB_6 (and LuB_6?) are superconductors while most other LnB_6 phases are antiferromagnetic at low temperatures [42]. In this connection it would be of interest to determine the lattice constants of the Sm compounds at low temperatures.

Normal valence compounds containing Ln^{3+} should be expected to be non-metallic, as is indeed observed for LnH_3 [38], $LnHal_3$ and Ln_2X_3 (X = chalcogen). The NaCl-type LnY compounds (Y = pnigogen) might also be non-metallic since their *d* band should be empty. From a plot of the lattice constants of the nitrides (Figure 1) we conclude that the valence state and hence the conduction type is the same for all nitrides with the exception of CeN. Reports on semiconductor-like behaviour of pressed powder samples of certain nitrides are contradicted by other investigations [16, 44]. Contamination with oxygen and deviation from stoichiometry seem to be the main reasons for the differences. Resistivity measurements [45] up to 500 °C on GdP and DyP single crystals also revealed a metallic behaviour, but the P deficiency of the samples well might have exceeded 5%. Similar results have been obtained by YAGUCHI [46] on pressed GdP, TbP and DyP powders. On the other hand, SCLAR [47] predicted energy gaps of the order of 2 eV for the nitrides and confirmed his data by diffuse-reflectance measurements. However, his values obviously refer to the gap due to the valence electrons engaged in the anion-cation bonds and do not exclude a superimposed metallic conduction in a narrow *d* band which we suppose to occur in anion-deficient samples. In fact, on the same powders SCLAR [47] measured metallic resistivities up to 1500 °C. The consistently occurring anion deficiency of the nitrides, phosphides and arsenides may be explained by assuming that the bottom of the *d* band lies slightly lower in energy than the top of the valence band. Deviations from stoichiometry would then be an intrinsic property of these phases. This explanation sounds reasonable for, say, LaN or TbN. However, the drastic change of the electronic structure that occurs on going from EuO to the isoelectronic neighbour GdN or from EuS to GdP, seems rather surprising. On the other hand, it would be surprising to find non-metallic TbC which is the next isoelectronic neighbour. The known NaCl-type rare-earth 'monocarbides' [14] reveal an even more pronounced anion deficiency while the mono-silicides and -germanides [14] are (metallic) polyanionic compounds, i.e. their anions display a valency less than 4 with respect to the cations.

In this connection we may mention the case of NaCl-type CrN (orthorhombic below its NÉEL point of 273 °K [48]). Although in stoichiometric CrN the cation has the very stable $d\varepsilon^3$ configuration, it is rather difficult to prepare the pure 1:1 phase and the resistivity reported for semiconducting CrN is surprisingly low [48]. In the phosphide the electronegativity difference seems to be too small; CrP crystallizes in an other structure and is metallic. We note that according to SCLAR's predictions [47] the energy gap due to the valence electrons vanishes for the rare-earth antimonides and bismuthides, so these compounds should be metallic even if stoichiometric. In non-transition-element compounds such a change of the conduction type would induce a structural change.

Several pnictides have been tested for superconductivity. ScN ($T_n = 1.4\,°K$) [29], YAs ($T_n = 0.31\,°K$) [50], YSb ($T_n = 1.02\,°K$) [29] and LaSb ($T_n = 1.02\,°K$) [29] were found to be normal down to the temperature reached, but LaN [51] was reported to reveal a definite though incomplete transition starting at 1.35 °K. Though one may have some reservations, superconductivity in this compound does not sound unreasonable since LaN_{1-x} has a partialy-populated *d* band and in this respect may be similar to superconducting $SrTiO_{3-x}$.

Because of the rapid increase of the 4*f* ionization energy with ionic charge tetravalent rare-earth ions can be expected to occur only at the beginning of a half-period, i.e. near Ce and Tb. In fact, Ce^{4+}, Pr^{4+} and Tb^{4+} exist in simple compounds such as the CaF_2-type dioxides CeO_2, PrO_2 and TbO_2 or the monoclinic ThF_4-type tetrafluorides CeF_4, PrF_4 and TbF_4 [52] while Nd^{4+} and Dy^{4+} were found only in complex salts such as Cs_3NdF_7 and Cs_3DyF_7 [10]. Such compounds, of course, are non-metallic [53]. From Figure 1 and 2 it follows that in Ce^{3+} the configurations f^1d^0 and f^0d^1 are not very different in energy [3]. In CeN the stabilization of the Ce $5d\varepsilon$ levels due to the crystal field and their broadening into a band due to direct interactions is sufficient to make it accessible for the excess cation electron. This phenomenon is observed also in metallic cerium [γ-Ce($a = 5.16$ Å) $\rightarrow$ α-Ce(p) ($a = 4.85$ Å)] as well as in other cerium compounds, e.g. in cubic Pu_2C_3-type Ce_2C_3, or in superconducting C15-type $CeRu_2$, but not in CeP or CeAs. The application of high pressure might be a means of transferring all the excess electrons in CeN into the *d* band²) and perhaps producing superconductivity, c.f. HfN [29]. Similar changes in the electronic configuration of rare-earth cations may be induced by pressure in compounds such as CeP, CeS, TbN, $NdBr_2$, TmI_2, CeH_2, EuH_2, etc. However, it is surprising that Ce_3N_4, the non-metallic nitride of tetravalent Ce, does not appear to exist. Attempts to synthesize Ce_3P_4 and Ce_3As_4, expected to crystallize in the Th_3P_4 type, also failed [45].

The presence of *f* and *d* electrons makes it possible that different properties can be produced for a given crystal structure by only slight variations of the constituent atoms. Thus, substitution of one third of the cations in Th_3P_4-type MLa_2S_4 provides transitions from a diamagnetic semiconductor (M = Yb, Sr, Ba) to a ferromagnetic semiconductor (M = Eu [55]), an antiferromagnetic metal (M = Gd, Tb), a superconductor (M = La [30]) and back to a diamagnetic ($M = La_{2/3}$) or paramagnetic ($M = Ce_{2/3}$) semiconductor.

In conclusion I would like to thank Dr. C. K. JØRGENSEN for helpful discussions.

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²) According to DIDCHENKO and GORTSEMA [16] the susceptibility of CeN is temperature-independent and Ce is tetravalent whereas BUSCH et al. [54] find a continuous increase of the susceptibility as the temperature approaches zero. From the lattice constant they conclude that only 70% of Ce are tetravalent (at room temperature). The thermal expansion of CeN is about twice that of LaN or PrN [44].

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Etude des solides par canalisation de particules à haute énergie

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Résumé. Revue brève de l'application des effets de canalisation et de blocage à l'étude des solides: détermination de l'orientation et de la symétrie du réseau, des potentiels interatomiques, de la concentration des interstitiels et de la structure des couches superficielles.

Lorsque des noyaux atomiques ou des ions de haute énergie se déplacent dans un réseau cristallin, l'interaction avec ce dernier peut être la même que dans la matière amorphe, si l'énergie des particules (keV ou MeV) est de plusieurs ordres de grandeur supérieure aux énergies caractéristiques du solide (au plus quelque 10 eV). Mais ce n'est plus le cas si la direction des particules est voisine d'une direction cristallographique principale: l'interaction est sujette alors à une anisotropie très marquée qui résulte de certains éléments de l'ordre cristallin. Les atomes du réseau, en étant disposés sur des plans et des chaînes parallèles, laissent entre eux des espaces presque libres formant des canaux parallèles. Ces derniers peuvent guider les particules, les «canaliser» par réflexion d'une paroi du canal à l'autre, de sorte qu'elles ne peuvent quitter ce dernier; pour cela, l'angle que fait la trajectoire avec l'axe du canal doit être assez faible, d'autant plus que l'énergie est plus grande. Ce phénomène a été découvert par des calculs numériques de trajectoires selon la méthode de Monte Carlo, puis il a été ensuite vérifié expérimentalement, donnant lieu à de nombreux travaux. L'effet a été décrit en détail dans divers articles de revue [1, 2] et même de vulgarisation [3], le traitement le plus complet étant celui de Datz *et al.* [4], de sorte que nous ne considérons ici que certains aspects particuliers, pouvant conduire à une application dans l'étude des solides.

L'anisotropie prononcée et fortement localisée au voisinage des directions principales suggère en premier lieu d'utiliser l'effet pour déterminer avec précision *l'orientation du réseau*, par exemple, d'une plaque monocristalline mince, bombardée parallèle-