is their unsatisfactory temperature stability and their relatively low flux density.

The material which has the potential to replace the ferrites in many applications is the Mn-Al-C alloy which was discovered as a permanent magnet material around 1958. The saturation magnetization and the temperature coefficients are more favourable than with the ferrites. It has been shown that the domain walls in this material are related to antiphase boundaries and crystal defects of various kinds. The τ-phase, which is not stable with temperature, is stabilized to some extent by the carbon addition. Unfortunately, this τ-phase does not grow uniaxially in the material and it is only by mechanical orientation through hot extrusion that some alignment of the magnetically easy axes can be achieved. In small quantities, this very promising material with energy product $(BH)_{max} \cong 5.5$ MGOe is available on the market. It seems that further development of the material or the extrusion process will be necessary.

BIBLIOGRAPHY

— Cullity B.D., *Introduction to Magnetic Materials* (Addison — Wesley) 1972.

— Schüler K. and Brinkmann K., *Dauermagnete* (Springer) 1970.

— Zijlstra H., "Trends in Permanent Magnet Material Development" *I.E.E.E. Trans. Magn.*, **MAG-14** (Sept. 1978) 5, pp. 661-664.

— Weinmann D., "Recoma-New Standards in Permanent Magnet Applications" *Goldschmidt informeirt* **2/79** 48, pp. 30-42.

— Livingston J.D., "Microstructure and Coercivity of Permanent Magnet Materials" *General Electric — Technical Information Series, Report No. 80, CRD 139,* July 1980.

Mixed Valence Compounds of the Rare Earths

A Fascinating Class of Solids

E. Müller-Hartmann, Cologne

(Institut für Theoretische Physik, Universität zu Köln)

The discovery of extraordinary substances or of new classes of substances with extraordinary properties has always added to the liveliness and relevance of solid state physics. One such class of unusual substances is certainly the mixed valence lanthanide compounds. Based upon them an important new branch of research in the field of magnetism has developed over the past decade which contains interesting implications for the understanding of condensed matter in general.

For some time it has been known that various rare earth compounds have lattice spacings with anomalous values. Since the ionic radii of the rare earths vary noticeably with their valence, it was obvious to chemists that something unusual had happened to the valence of the rare earths in these compounds. However, it was not before the late sixties that physicists fully appreciated that these compounds were exotic solids.

The characteristic common feature of mixed valence compounds is believed to be that their rare earth constituents are not in a stable state of well defined valence, but coexist in two different valence states corresponding to two distinct atomic configurations of the 4f-shells, e.g. $4f^n$ and $4f^{n-1}$. It is furthermore believed that the two configurations are not associated with different lattice sites — this would be called an inhomogeneously mixed valence — but that both of them are found on each rare earth atom in the compound: the valence is homogeneously mixed.

In the Table overleaf, a representative list of mixed valence compounds is given; some thirty known compounds appear to have mixed valence at normal pressure, others go into a mixed valence state at high pressure. Not included in the Table are the numerous mixed valence alloys and rare earth impurities with mixed valence in various environments.

Evidence for the coexistence of two different 4f-configurations is derived through several experimental methods. The most direct evidence probably comes from X-ray photoelectron spectroscopy (XPS) where the spectrum of the photoelectrons directly reflects the excitation spectrum of the 4f-configurations left behind, i.e., $4f^{n-1}$ and $4f^{n-2}$. Unfortunately, such evidence cannot be obtained for all compounds in question. In particular, XPS analysis does not apply to Ce metal and its compounds, as it is impossible to draw photoelectrons out of the configuration $4f^0$. This leads to some uncertainty whether all the compounds listed in the Table have two coexisting 4f-configurations. However, there is overwhelming evidence that the majority of compounds listed contain two configurations of their rare earth 4f-shells.

A second body of evidence is needed to support the assumption of homogeneous valence mixing. Various properties of the compounds point in this direction. Again, there is a method which is particularly well suited to distinguish between inhomogeneous and homogeneous mixing: Mössbauer spectroscopy identifies 4f-configurations, as the chemical shift varies with the

Normal Pressure		High Pressure
$Ce\ Pd_3$	$Eu_3\ S_4$	Ce
$Ce\ Ni_2\ Ge_2$	$Tm\ Se$	$Ce\ Al_2$
$Ce\ Sn_3$	$Yb\ Al_2$	Pr
$Ce\ Ni_5$	$Yb\ Al_3$	$Sm\ S$
$Ce\ Cu_2\ Si_2$	$Yb\ Pd_3$	$Sm\ Se$
$Ce\ N$	$Yb\ Cu_2\ Si_2$	$Sm\ Te$
$Ce\ Be_{13}$	$Yb\ Cu\ Al$	Eu
$Ce_2\ C_3$	$Yb\ In\ Au$	$Eu\ O$
$Sm\ B_6$	$Yb\ Ni_2\ Ge_2$	$Eu\ Pt_3$
$Sm\ O$	$Yb\ In\ Au_2$	$Tm\ Te$
$Sm_3\ S_4$	$Yb\ In\ Pd$	$Yb\ S$
$Eu\ Cu_2\ Si_2$	$Yb\ Zn_2\ Sb_2$	$Yb\ Se$
$Eu\ Pd_2\ Si_2$	$Yb\ Zn_2\ As_2$	$Yb\ Te$
$Eu\ Rh_2$	$Yb\ Zn_2\ P_2$	

configuration. For mixed valence compounds a single narrow Mössbauer line is observed between the positions at which the lines of the two coexisting configurations are expected. This represents unequivocal evidence for homogeneous valence mixing of the corresponding compound.

The above brief discussion is meant to demonstrate that there can be no doubt about the existence of rare earth compounds with homogeneously mixed valence. The reader may now argue: What is so unusual about that? After all, mixing of atomic configurations is a very common phenomenon in chemistry and solid state physics. Not only are valence electrons in solids never in identifiable atomic configurations, but also 3d- and 4d-shells assume mixed configurations, e.g., in the classic cases of the metals Ni and Pd. Thus, what is it that makes rare earth mixed valence compounds worth mentioning?

The answer to this question becomes obvious from an inspection of the atomic orbitals of rare earth atoms. Fig. 1 gives an impression of the radii of rare earth orbitals. The remarkable feature to be noticed is that the 4f-shell is deeply buried in the Xenon core ($Xe = Kr\ 4d^{10}\ 5s^2\ 5p^6$). The radius of the 4f-orbitals is four to five times smaller than the atomic radius. Such an extreme localization of a partially filled shell is not found anywhere else in the periodic table.

The exceptionally small size of 4f-orbitals implies a clear-cut hierarchy of energies for rare earth compounds. Coulomb interactions between 4f-electrons within a single rare earth are particularly large due to the small mutual distance between these electrons. It is therefore not surprising that the intraionic energies of the 4f-shell are the largest energies involved. One of these is the 4f-4f Coulomb repulsion which may be identified with the energy required for the excitation

$$4f^n + 4f^n \rightarrow 4f^{n-1} + 4f^{n+1} \qquad (1)$$

and which has (screened) values of almost 10 eV. Other intraionic energies are the exchange and spin-orbit splittings between the various states of a 4f-configuration which are well known from atomic physics and which are a few eV and (with the exception of $4f^6$) a few tenths of an eV, respectively. All these ionic energies are larger than those which the 4f-electrons encounter due to their coupling to the other degrees of freedom of the solid. In particular, the overlap between 4f-orbitals on different rare earth ions is so small that in most cases any direct contribution to the 4f-band width is negligible. The overlap between 4f-orbitals and conduction band states is also rather weak due to the small 4f-radius. This overlap causes a hybridization of 4f-orbitals with conduction band states and is the primary source of a broadening of 4f-states. In any case, the clear hierarchical separation of intraionic from coupling to solid energies excludes a description of 4f-electrons in terms of an independent particle approximation. There is no question that 4f-shells have to be visualized via an ionic model.

We now have to consider the elementary process:

$$4f^n \rightarrow 4f^{n-1} + e \qquad (2)$$

where an electron leaves the 4f-shell and goes into a conduction band. The lowest energy required for this process is obtained if the electron goes into the lowest available band state, i.e. onto the Fermi surface. It is obvious that the value of this energy will be decisive for the stability of the configuration $4f^n$. If it is an eV or so, then the rare earth ion will be quite stable against process (2) and the configuration $4f^n$ will be quite pure. If it is much smaller, of the order of the thermal energy or of the hybridization induced broadening of the state $4f^n$, then the configuration $4f^n$ is unstable and will be mixed with the configuration $4f^{n-1}$. This is the situation which leads to mixed valence compounds. Thus, it is the minimum energy required for process (2) which decides if a compound has mixed valence or not.

More than two configurations of a 4f-shell can never coexist. This follows easily from combining processes (1) and (2): If (2) is possible at no cost of energy, then the transitions $4f^n + e \rightarrow 4f^{n+1}$ as well as $4f^{n-1} \rightarrow 4f^{n-2} + e$ require the same large energy as (1) and are dynamically forbidden. In a band model of 4f-electrons, the single site occupation numbers would have a much broader distribution. Thus, the limitation to, at most, two coexisting configurations is an obvious consequence of the ionic description of the 4f-shells.

From what was said above it is evident that in contrast to conventional rare earth compounds, mixed valence compounds permit electrons to jump on and off 4f-orbitals. A typical process resulting from this is the following: an electron leaves a 4f-shell by jumping into the conduction band and then moves on by jumping into the 4f-shell of a neighbouring 4f-atom. A concise way of phrasing this effect is to say that mixed valence provides 4f-shells with translational degrees of freedom in addition to the rotational degrees of freedom which they usually have.

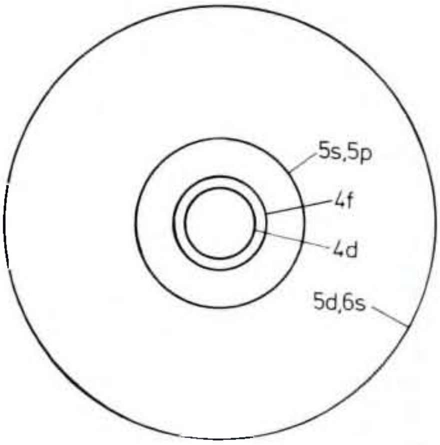

Fig. 1 — A schematic diagram of the radii of the rare earth orbitals.

The dominant dynamical mechanism which drives the valence change (2) and which thus activates the translational degrees of freedom is the hybridization of the 4f-orbitals with conduction band states. It is the primary source of a band width associated with the motion of electrons between 4f-shells. As discussed above, this band width is rather small due to the small size of the 4f-orbitals. It is of the order of a hundredth of an eV.

Summarizing the above discussion we are now in the position to appreciate one of the basic reasons why mixed valence compounds are so interesting. For one thing, only in these compounds are electrons able to move from one 4f-shell to another. Second, the band width associated with this motion is much smaller than the correlation energies of the 4f-shells. Mixed valence compounds thus represent a sizable class of solids with itinerant electrons in the narrow band (or high correlation) limit. To understand the significance of this statement one should realize how different the situation is for transition metals which are commonly considered narrow band systems. For transition metals the correlation energy is comparable to, but nevertheless somewhat smaller than the band width, whereas in mixed valence compounds it is one hundred times larger. This comparison shows that mixed valence compounds of the rare earths open an unprecedented opportunity to study systematically the behaviour of itinerant electrons in the limit of very high correlation or very heavy effective masses.

What are the lessons which can be learned from studying these unusual solids? Some possible answers to this question are given in what follows.

The magnetic properties of mixed valence compounds are very different from those of ordinary rare earth compounds which always have some kind of magnetic long range order at low temperatures. Mixed valence compounds do not appear to show magnetic long range order or any kind of magnetic phase transition at any temperature. The only exception to this rule is the compound TmSe which orders magnetically at a few Kelvin. For a discussion of the exceptional role of TmSe it is important to know that this is the only mixed valence compound with a magnetic ground state in each of the coexisting configurations. All the other rare earths which have been found to form mixed valence compounds, i.e. Ce, Sm, Eu, and Yb, happen to mix one magnetic with one nonmagnetic singlet ground state. It is very regrettable that TmSe is the only mixed valence Tm-compound known, because more evidence is needed to establish that the aspect pointed out above is decisive for the magnetic behaviour. Praesodymium metal which also mixes two magnetic configurations would be another welcome candidate to be investigated. Unfortunately, the mixed valence phase of Pr exists only at such high pressures that magnetic measurements are not feasible. In any case, the evidence on magnetic properties strongly supports the following general statement: Extremely narrow bands have a non-magnetic ground state if they mix a magnetic and a singlet ground state via hybridization with conduction bands. Despite some promising progress in the theory of mixed valence compounds, a deep understanding of this rule is still lacking.

If the ground state of mixed valence compounds is not magnetic, what then is its electronic structure like? The low temperature properties observed, all point in the same direction: the magnetic susceptibility and the specific heat, e.g., both strongly enhanced in comparison with conventional metals, seem to indicate a Fermi liquid behaviour with a rather low Fermi temperature. In fact, all the evidence on magnetic, caloric and transport properties suggests that we are dealing with superheavy Fermi liquids. This is another intriguing aspect, since it allows one to study charged Fermi liquids in a new range of parameters not accessible with usual conduction electrons. The heavy Fermions found are naturally associated with the narrow 4f-bands described above. That the mass of these Fermions is large, namely, more than one hundred times the free electron mass, is not surprising. It is rather to be expected regarding the 4f-band widths given above and realizing that "narrow band width" is synonymous with "heavy mass" or "low Fermi temperature". In terms of a microscopic description, the Fermi liquid ground state contains intricate quantum correlations associated with the coherent mixing of the coexisting ionic configurations.

Mixed valence compounds do not become superconducting at low temperatures. This is to be considered both an interesting and an unfortunate fact. It is interesting, because metals are known to "strongly dislike" a normal Fermi liquid ground state. A majority of them indeed become superconducting. Most of the rest avoid superconductivity only by means of magnetism. Perhaps mixed valence compounds have found their own way of surviving as normal Fermi liquids.

The absence of superconductivity is unfortunate, because its presence might have provided a chance to study the superconductivity of heavy Fermi liquids. There is, in fact, one single mixed valence compound, $CeCu_2Si_2$, for which there is strong evidence for superconductivity. This is a fascinating exception — all the more since it shows heavy-fermion superconductivity. The further investigation of $CeCu_2Si_2$ may be hoped to yield interesting insight into this topic.

Electron-Phonon Coupling

The discussion of superconductivity leads us to the subject of electron-phonon interactions. In ordinary solids, the motion of the ions can be clearly separated from the motion of the electrons in terms of the adiabatic approximation, since ions are so much heavier than electrons. Even in metals where it is very easy to excite electrons, the large mass ratio is extremely helpful for understanding the consequences of electron-phonon coupling. For mixed valence compounds, however, the benefit of a large mass ratio is obviously lost, because the valence fluctuations (2) which we have identified as heavy Fermions are at least one hundred times heavier than conventional conduction electrons. It therefore has to be expected that our heavy Fermi liquids have non-adiabatic interactions with the lattice vibrations. In a few compounds, anomalous phonon broadening has, in fact, been found.

The strength of the electron-phonon coupling can be judged from an important effect which is also responsible for the anomalous lattice spacings mentioned earlier. Due to their small orbital radii 4f-electrons are very effective in screening the nuclear charge. Therefore the atomic radii of the rare earths, i.e. the radii of their 5s, p-shells and those of their valence orbitals, shrink by some five percent in the process (2). Correspondingly large displacements of the neighbouring ions follow. This sizable effect causes a strong coupling of valence fluctuations to certain motions of the ions. It also explains the anomalously large compressibility of mixed valence compounds.

Let these few remarks on the electron-phonon interaction be sufficient to indicate that mixed valence compounds are unusual solids with respect to their lattice properties, too. It seems that the observation of lattice anomalies in these compounds is a rather delicate matter and the anomalies presently identified may be only the tip of an iceberg.

It was the aim of the above exposition to call special attention to some aspects of mixed valence compounds which may be expected to be of general interest. Needless to say, there are many more features to those compounds which are fascinating the experts. It also has to be qualified that not all of the compounds listed in the Table fit easily into the unified scheme developed above. In any case, mixed valence compounds will be an interesting subject of research for years to come.

The interested reader may be willing to look closer into the subject. For this purpose the conference proceedings (1) and the reviews (2) and (3) are recommended.

REFERENCES

1. Falicov L.M., Hanke W. and Maple M.P. (Eds.), *Valence Fluctuations in Solids* (North-Holland) 1981.

2. Lawrence J.M., Riseborough P.M. and Parks R.D., *Rep. Prog. Phys.* **44** (1981) 1-84.

3. Grewe N., Leder H.J. and Entel P. in: Treusch J. (Ed.), *Festkörperprobleme XX* (Vieweg) 1980.

EPS Associate Members

Battelle Geneva Research Center, Carouge-Geneva, Switzerland

Brown, Boveri & Company, Ltd. Baden, Switzerland

Cerberus Ltd., Maennedorf, CH

CERN — European Organization for Nucl. Res., Geneva, Switzerland

Comitato Nazionale per l'Energia Nucleare, Frascati, Italy

Commissariat à l'Energie Atomique, Paris, France

* Compagnie de Saint-Gobain, Paris, France

* Compagnie Française Philips, Paris, France

Consiglio Nazionale delle Ricerche, Rome, Italy

DESY — Deutsches Elektronen-Synchrotron, Hamburg, FRG

* Electricité de France, Paris, France

European Space Agency, Paris, France

FIZ — Fachinformationszentrum, Eggenstein-Leopoldshafen, FRG

FOM — Foundation for Fundamental Res. on Matter, Utrecht, NL

General Electric Co. Ltd., Wembley, England

Gesellschaft für Schwerionenforschung, mbH, Darmstadt, FRG

Hahn-Meitner-Institut, Berlin, FRG

IBM Europe, Paris, France

Institut Max von Laue-Paul Langevin, Grenoble, France

Istituto Nazionale di Fisica Nucleare, Rome, Italy

Cont. overleaf