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Metal–Metal Bonding in Y_2Cl_3—A NMR and Magnetic Susceptibility Study

R. K. KREMER, HJ. MATTAUSCH, AND A. SIMON

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-7000 Stuttgart 80, Federal Republic of Germany

AND S. STEUERNAGEL AND M. E. SMITH*

Bruker Analytische Messtechnik GmbH, Silberstreifen, D-7512 Rheinstetten 4, Federal Republic of Germany

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The electrical properties as well as the static and the dynamic magnetic behavior of Y_2Cl_3 and YCl_3 were investigated with the help of powder DC susceptibility and magic angle spinning NMR measurements. Y_2Cl_3 is a semiconductor with a band gap of 0.85 eV, and is diamagnetic above 100 K. The ^{89}Y resonance in Y_2Cl_3 exhibits considerable paramagnetic chemical shifts, +762 ppm and +506 ppm, which are distinctly different for the two Y lattice sites, and contrast the shift of −230 ppm for anhydrous YCl_3. These features are related to metal–metal bonding in Y_2Cl_3.

Introduction

The stochiometric compound Gd_2Cl_3 was the first example to show a rare earth (RE) metal in an oxidation state below +2 ("sesquichloride") (*1–3*). Further synthesis and characterization identified the compounds Tb_2X_3 (X = Cl, Br), Gd_2Br_3, and also the nonmagnetic Y_2Cl_3 (*4*). The high metal content of the RE sesquihalides produces a new crystal structure type which is very anisotropic as it contains parallel chains of trans-edge sharing metal octahedra that are embedded in and charge balanced by the halogen atom environment (Fig. 1).

A single metal octahedra chain itself (Fig. 2) can be constructed via a transedge "condensation" of RE_6 octahedral clusters into an (ideally) infinite chain structure (Fig. 2) (*5*).

The metal octahedra chains are separated from one another by intervening halogen atoms: Chains of halogen atoms along [010] of the monoclinic cell bridge the apices of the octahedra thus forming sheets of octahedra chains parallel to $(20\bar{1})$ which are separated from neighboring ones by double layers of halogen atoms capping the triangular faces of the metal octahedra.

A clear hierarchy for the metal–metal dis-

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* Present address: C.S.I.R.O. Division of Materials Science and Technology, Locked Bag 33, Clayton, Victoria 3168, Australia.

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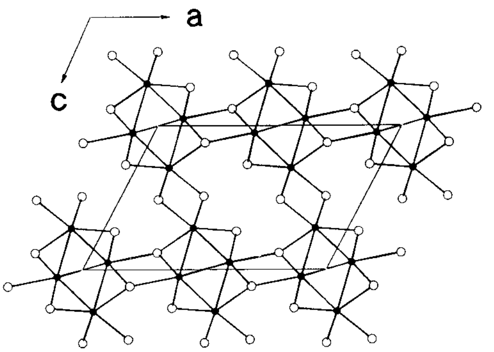

FIG. 1. Structure of Y_2Cl_3 projected down [010] of the monoclinic cell. Full circles: Y atoms; open circles: Cl atoms.

tances within and between neighboring octahedra chains is found in the RE_2X_3 structure. For example, in Y_2Cl_3, which is the object of our investigation, distances between metal atoms in neighboring chains are greater than 443.1 pm, while distances between metal atoms in the same octahedra chain are less than 369.4 pm (*6*). Most significantly, the octahedra are distinctly compressed along the shared edge and this Y1–Y1′ distance of 326.6 pm is the shortest metal–metal distance observed in Y_2Cl_3.

The main question in the field of these metal-rich RE halides concerns the special role of those electrons which are not necessary to satisfy the valence of the halide ions. In the case of the lanthanoids localization into the $4f$ shell could be ruled out since high temperature susceptibility measurements, as for Gd_2Cl_3, proved that the magnetic moment per Gd atom corresponds to that of a half-filled $4f^7$ configuration, as is usually found for Gd and all its compounds (*7*).

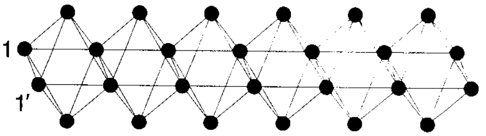

FIG. 2. Chain of trans edge sharing metal octahedra extracted from the structure of Y_2Cl_3. 1 and 1′ label the metal atoms in a shared edge.

The formation of metal–metal bonds was considered very likely in view of the short metal–metal distances within an octahedral chain. However, the early assumption that the electrons are delocalized in a one-dimensional band with good metallic conductivity along the chains could not be confirmed. Instead of this, it was shown by photoelectron spectroscopy and conductivity studies that Gd_2Cl_3 and Tb_2Cl_3 are semiconductors with bandgaps of about 1 eV (*8*).

According to LCAO band structure calculations for a $[Gd_4Cl_4]_\infty$ chain, the bandgap is the result of an avoided crossing of metal *d* bands having identical symmetry characteristics. Three *d* bands that are strongly metal–metal bonding along the shared *M*1–*M*1′ edge (Fig. 2) are split off from the block of the rest by a gap of about 0.7 eV (*9*). The surplus of three metal *d* valence electrons exactly fulfills the requirement to completely fill the three low-lying metal–metal bonding bands and semiconducting behavior results. Metal–metal bonding to the apical metal atoms or along the chains is less pronounced. In terms of these band structure calculations the alternative description of the crystal structure as a ladder sequence of strongly bonded Gd–Gd dimers capped by the more distant apical Gd atoms bears some justification (*2*).

We have performed ^{89}Y NMR on Y_2Cl_3 and the parent compound YCl_3 and determined the isotropic chemical shifts using magic angle spinning (MAS) to improve the accuracy by removal of the anisotropic contributions (*10*). Chemical shifts originating from magnetic shielding due to the internal electronic currents can provide valuable, in particular, site sensitive, information about the electronic distribution and chemical bonding in a compound (*12*).

The magnetic susceptibility as a bulk quantity, which is sensitive to the chemical bonding, was measured in Y_2Cl_3 and compared to YCl_3. Finally, the temperature dependence of the electrical resistivity of Y_2Cl_3 was determined to see whether Y_2Cl_3, like Gd_2Cl_3, exhibits a localized electronic system.

Experimental

Sample Preparation

YCl_3 was prepared from Y_2O_3 (99.99%, Universal Matthey) by reaction with NH_4Cl (p.a. Merck) (*13*) and purified by two distillations in tantalum crucibles under high vacuum. Coarse crystalline powder of Y_2Cl_3 was synthesized from stoichiometric mixtures of the chipped metals (metal purity 99.99%, from Johnson Matthey) and the trichloride YCl_3 following a method described in detail previously (*6*). Y_2Cl_3 are moisture sensitive and all handling of the samples was done under dried inert gas atmospheres.

Electrical Conductivity

The resistance of Y_2Cl_3 was determined on an *in situ* pressed pellet with a two point electrometer method. The press was made from a STENNAN cylinder and stainless steel pistons and heated in a temperature regulated tube furnace which was attached to an argon glove box.

Magnetic Susceptibility

The susceptibilities of powder samples with typical masses of 100 mg were determined with a SQUID magnetometer. The samples were contained in carefully dried gelatin capsules the susceptibilities of which were measured in separate runs and corrected for.

For fixed temperatures the susceptibilities were taken in external magnetic fields ranging from 1 to 5 T. Honda–Owen plots were performed to correct for ferromagnetic impurities (*14*). Finally, a χ_{mol} versus $1/T$ plot according to (1) and the extrapolation $T \to \infty$ allowed an estimate of the contribution arising from spurious paramagnetic impurities,

$$\chi_{mol} = C/T + \chi_0. \quad (1)$$

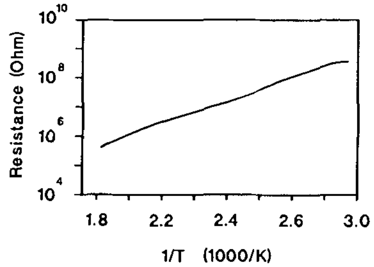

FIG. 3. Resistance of a pressed powder pellet of Y_2Cl_3 as function of the inverse temperature.

Nuclear Magnetic Resonance

NMR was measured with a Bruker MSL 400 spectrometer at room temperature in a magnetic field of about 9.4 T corresponding to a resonance frequency of about 19.6 MHz for the ^{89}Y nuclei ($\gamma/2\pi$ = 2.086 MHz/T). The moisture sensitive samples were filled in sealed plexiglas capsules which were contained in 7 mm diameter zirconium oxide spinners. Five thousand free induction decays (FID) after pulses of 5 μsec ($\sim\pi/6$) with a repetition time of 10 sec were acquired. MAS frequencies were between 3 and 4 kHz. The low resonance frequency for ^{89}Y even in this high magnetic field means ringing causes corruption of the early part of the FID and ~50 μsec was removed prior to Fourier transformation. The resonance fields were referenced against the resonance of ^{89}Y in a 1 *M* YCl_3 aqueous solution standard.

Results and Discussion

The conductivity experiments on Y_2Cl_3 prove semiconducting behavior. The room temperature resistance of the pellets typically was of the order of 10^8 to 10^9 Ω and decreased by several orders of magnitude on heating to 650 K. Figure 3 shows the

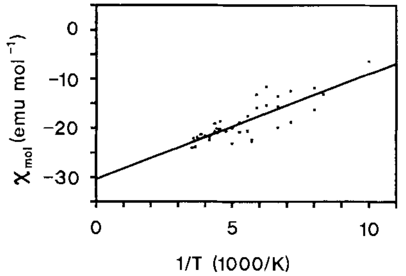

FIG. 4. Molar magnetic susceptibility of a powder sample of Y_2Cl_3 after correction for ferromagnetic impurities. The straight line was obtained from a least-squares fit with parameters as given in the text.

temperature dependence of the resistance of a Y_2Cl_3 pellet in a log R versus $1/T$ plot from which a bandgap of 0.85(5) eV was deduced.

This result gives very similar gap values to those observed for pellets and single crystals of Gd_2Cl_3 and Tb_2Cl_3 (*8*) and confirms what is implied by the structural similarities. Chemical bonding in Y_2Cl_3, Gd_2Cl_3, and Tb_2Cl_3 is essentially the same so that conclusions obtained here should be applicable also to the other known sesquihalides.

The susceptibility of the investigated sample of Y_2Cl_3 demonstrates that Y_2Cl_3 is diamagnetic above about 100 K (Fig. 4). Spurious impurities give rise to a small additional paramagnetic susceptibility contribution which follows a Curie-like temperature dependence as shown by the straight line in the χ_{mol} versus $1/T$ plot in Fig. 4. The extrapolation $T \rightarrow \infty$ yields a diamagnetic susceptibility of $\chi_0 = -31(1) \times 10^{-6}$ emu mol^{-1}. The slope C of about 25×10^{-4} emu K mol^{-1} corresponds to 0.7% spin $S = \frac{1}{2}$ impurity particles per mol Y_2Cl_3 or equivalently 160 ppm Gd ($S = \frac{7}{2}$) impurity atoms per one Y atom.

Similar data analysis for YCl_3 results in $\chi_0 = -79(1) \times 10^{-6}$ emu mol^{-1} in good agreement with -82×10^{-6} emu mol^{-1} one obtains by summing the diamagnetic increments from the constituent elements: -12×10^{-6} emu mol^{-1} for Y^{3+} and -23.4×10^{-6} emu mol^{-1} for Cl^- (*15*).

According to this result the diamagnetic contribution for Y_2Cl_3 (one extra Y atom in addition to YCl_3) is estimated to $\chi_{dia} = -91 \times 10^{-6}$ emu mol^{-1}. The experimental finding thus reveals a temperature independent paramagnetic contribution to the susceptibility of Y_2Cl_3 of $\delta\chi_{TIP} = +60 \times 10^{-6}$ emu mol^{-1}.

The diamagnetic susceptibility found for Y_2Cl_3 clearly confirms what has been concluded for Gd_2Cl_3, that the excess valence electrons are not localized into inner atomic shells but rather are involved in the metal–metal bonding (*7, 20*). Unpaired electrons should show a paramagnetic Curie-like susceptibility which in the case of Gd_2Cl_3 was difficult to distinguish from the overwhelming paramagnetic background susceptibility of the 4*f* electrons.

The NMR spectrum of Y_2Cl_3 consists of two narrow resonance lines apparently originating from ^{89}Y nuclei on the two different lattice sites in Y_2Cl_3 occupied by Y atoms

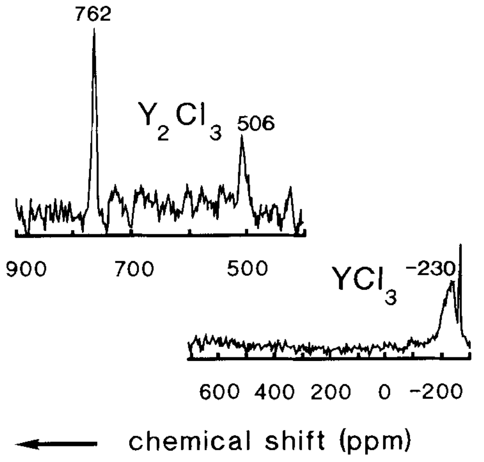

FIG. 5. ^{89}Y NMR spectra of Y_2Cl_3 and YCl_3. The sharp spike near −270 ppm is an artifact caused by an external frequency. The shifts are referenced against the resonance of ^{89}Y in a 1 *M* aqueous solution.

(Fig. 5). They are shifted by +762 ppm and +506 ppm relative to the standard aqueous solution of YCl_3 (*16*). In YCl_3 all Y atoms occupy the same lattice site and correspondingly only one line is detected at −230 ppm. The resonance line of ^{89}Y in YCl_3 is significantly broader than the lines in Y_2Cl_3.

The small gyromagnetic ratio of ^{89}Y has meant that few studies of the influence on the chemical shift of yttrium have been done especially in the solid state. The positive chemical shifts of the ^{89}Y resonances in Y_2Cl_3 are noteably large and come near to the magnitude of typical Knight shift values detected for metallic compounds, e.g., for YH_2 (*17*).

In the limited range of diamagnetic, insulating solids investigated so far, a shift range of ~370 ppm has already been observed (*18*, *19*). Hence the much larger ^{89}Y shift between these structurally very different compounds, anhydrous YCl_3 and Y_2Cl_3 is not surprising. Also it has been noted that the linewidth in MAS NMR experiments shows a wide variation, with more than a tenfold change in yttrium aluminates of comparable crystallinity. This behavior was attributed partially to averaged dipolar interactions with ^{27}Al that depend on the size of the quadrupolar interaction at the aluminium nucleus (*19*). A similar effect with the close Y–Cl distances and the quadrupolar character of chlorine could be applicable for the present compounds.

Generally, the chemical shift and the magnetic susceptibility are tensor quantities which usually are split into a sum of a *diamagnetic* part that reduces the external field and a *paramagnetic* part that enhances the external magnetic field. In the sense of second order perturbation theory the paramagnetic shift and susceptibility arise from a Van Vleck-like admixture of excited states into the ground state and an *unquenching* of its angular momentum. The diamagnetic chemical shift and the susceptibility tensor involves ground state wavefunctions only (*21*).

Since the MAS NMR experiment only determines the trace of the shielding tensor and moreover the powder susceptibility averages the two lattice sites we do not have sufficient experimental information to allow an assignment of the resonances in Y_2Cl_3. In particular, anisotropies of the shift tensor that would allow an unambiguous assignment of the resonances to the two lattice sites are not available since the low sensitivity of ^{89}Y means obtaining an adequate signal-to-noise ratio for the static spectra would require a prohibitive amount of time.

Nevertheless, some qualitative conclusions are possible: First of all, there is the clear differentiation of the chemical shifts for the two lattice sites in Y_2Cl_3 which corroborates the band structure calculations predicting a different degree of metal–metal bonding for the two metal atom sites in the sesquihalides.

Second, the strong paramagnetic chemical shifts must be related to the additional metal–metal bonding states about 1 eV below the unoccupied metal *d* bands. These states are mainly associated to metal–metal bonding in the shared edge in the metal octahedra chain and they represent the essential difference compared to the band structure of the ordinary trichlorides. The overall energy splitting of the empty metal *d* bands and the filled halide *p* bands in the sesquihalides is about 5 eV and thus nearly identical to the ionic gap found, e.g., for $LaCl_3$ (*22*).

According to Ramsey's formula the paramagnetic shifts depend on the mixing matrix elements but also are inversely proportional to the energy separation of the excited states. Consequently, the small energy gap between the metal–metal bonding states and the empty *d* states should promote a very effective admixture of empty *d* states and in this way cause strong paramagnetic shifts and induced paramagnetic moments for the sesquihalides. Along this line, we tentatively assign the ^{89}Y resonance signal displaying the largest paramagnetic shift to those Y atoms located in the shared edge of the octahedra chain.

The paramagnetic susceptibility obtained for Y_2Cl_3 after correction for the diamagnetic core contribution is interpreted as a Van Vleck contribution and taken as indication for the presence of localized metal–metal bonding. Even more pronounced temperature independent paramagnetism induced by the admixture of excited metal–metal bonding states is observed as a common property of reduced transition metal halides and has been investigated in more detail for the compounds Nb_6I_{11} and HNb_6I_{11} (*23*).

In summary, we have determined the electrical properties as well as the static and the dynamic magnetic behavior of Y_2Cl_3 and YCl_3 with the help of powder DC susceptibility and MAS NMR measurements. According to the temperature dependence of the resistivity, Y_2Cl_3 is a semiconductor with a band gap of 0.85 eV. The magnetic properties of Y_2Cl_3 relative to those of YCl_3 are characterized by considerable paramagnetic chemical shifts, significantly different for the two different Y lattice sites, and a sizeable paramagnetic contribution to the magnetic susceptibility. These features are linked to the presence of additional occupied metal–metal *d* bonding states in the band structure of Y_2Cl_3.

Acknowledgments

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References

1. D. A. Lokken and J. D. Corbett, *J. Am. Chem. Soc.* **92,** 1799 (1970).
2. D. A. Lokken and J. D. Corbett, *Inorg. Chem.* **12,** 556 (1973).
3. A. Simon, N. Holzer, and Hj. Mattausch, *Z. Anorg. Allg. Chem.* **456,** 207, (1979).
4. For a recent review of the chemical and physical properties of the metal-rich halides of the rare earths see A. Simon, Hj. Mattausch, G. J. Miller, W. Bauhofer, and R. K. Kremer, *in* "Handbook on the Physics and Chemistry of Rare Earths," Vol. 15, (K. A. Gschneidner, Jr., and L. Eyring, eds.), North-Holland, Amsterdam, in press.
5. A. Simon, *Angew. Chem.* **93,** (1981); *Angew. Chem. Int. Ed. Engl.* **20,** (1981).
6. Hj. Mattausch, J. B. Hendricks, R. Eger, J. D. Corbett, and A. Simon, *Inorg. Chem.* **19,** 2128 (1980).
7. J. D. Greiner, J. F. Smith, J. D. Corbett, and F. J. Jellinek, *J. Inorg. Nucl. Chem.* **28,** 971 (1966).
8. W. Bauhofer and A. Simon, *Z. Naturforsch. A* **37,** 568 (1982); G. Ebbinghaus, A. Simon, and A. Griffith, *Z. Naturforsch A* **37,** p. 564 (1982).
9. D. W. Bullet, *Inorg. Chem.* **19,** 1780 (1980); D. W. Bullet, *Inorg. Chem.* **24,** 3319 (1985).
10. YCl_3 crystallizes in the monoclinic $AlCl_3$ structure type (space group C2/m) which is a distorted NaCl structure with only one third of the possible metal atom positions filled. In YCl_3 all Y atoms have the same crystallographic environment (*11*).
11. D. H. Templeton and G. F. Carter, *J. Phys. Chem.* **58,** 940 (1954).
12. See, e.g., M. Mehring, "Principles of High Resolution NMR in Solids," 2nd ed. Springer-Verlag, Berlin Heidelberg New York (1983).
13. C. Meyer and P. Ax, *Mater. Res. Bull.* **17,** 1447 (1982).
14. K. Honda, *Ann. Phys.* **32,** 1027 (1910); M. Owen, *Ann. Phys.* **37,** 657 (1910).
15. P. W. Selwood, "Magnetochemistry," Interscience, New York (1943); A. Earnshaw, "Introduction to Magnetochemistry," Academic Press, New York (1968).
16. Positive shifts in our notation correspond to decreasing shielding from the magnetic field.
17. D. S. Schreiber, *Phys. Rev. A* **137,** 860 (1965).
18. A. R. Thompson and E. Oldfield, *J. Chem. Soc. Chem. Commun.* 27, (1987).
19. R. Dupree and M. E. Smith, *Chem. Phys. Lett.* **148,** 41 (1988).
20. R. Kremer, Thesis, TU Darmstadt, 1985, unpublished.
21. N. F. Ramsey, *Phys. Rev.* **78,** 699 (1950); J. H. Van Vleck, "Electric and Magnetic Susceptibilities," Oxford Univ. Press, London/New York, (1932).
22. D. M. Gruen, J. G. Conway, and R. D. McLaughlin, *Chem. Phys.* **25,** 1102 (1956).
23. A. Simon, *Z. Anorg. Allg. Chem.* **355,** 311 (1965); J. J. Finley, H. Nohl, E. E. Vogel, H. Imoto, R. E. Camley, V. Zevin, O. K. Andersen, and A. Simon, *Phys. Rev. Lett.* **46,** 1472 (1981); J. J. Finley, R. E. Camley, E. E. Vogel, V. Zevin, and E. Gmelin, *Phys. Rev. B* **24,** 1323 (1981).