true for alloys of metals in the same column of the periodic table. For alloys between transition elements in neighbouring columns but different rows there may well exist rather fine balance between the "collective band" and virtual bound state situations; and we tentatively suggest that there exists an excited state of the *Rh* - Fe system in which virtual bound states are associated with the iron atoms, which then give much stronger scattering of conduction electrons than in the ground state where no strong resonance exists for electrons at the Fermi level. Such virtual bound states have been discussed extensively by Friedel [4], and for transition metal-iron alloys by Clogston et al. [6] and Anderson [7]. The alternative possibility (which has been considered in general terms by White and Clogston [8] of an excitation of a virtual bound state from a magnetized to an unmagnetized condition, although consonant with the resistivity of the *Rh* - Fe alloys, seems very difficult to reconcile with the magneto-resistance data. From their susceptibility data Clogston et al. [6] concluded that iron possessed a magnetised virtual bound state in solution in rhodium, but the adjustment required for their data to yield a moment may be indicative of a more complicated situation.

When the conductivity is a strong function of electron energy large thermo-electric powers are to be expected. We have measured the thermoelectric power S of the rhodium 0.5 at. % iron alloy relative to a silver 0.37 at. % gold alloy, and find that $-S$ increases steadily as the temperature is *decreased* below 50°K (where it is about zero), reaching values of 2.7, 3.6, 4.1 and 4.6 microvolts/degree at 10°, 5°, 3° and 1.5°K respectively. This behaviour again is very unusual, for even in the *Cu* - Fe alloys where "giant" thermo-powers are found [9] these tend towards zero for 0°K in the 4° - 1°K range.

Further details of these and other measurements on rhodium-iron and iridium-iron alloys (where related behaviour is found) will be given elsewhere. It seems likely that these materials could form very useful resistance thermometers down to very low temperatures.

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HALL-MEASUREMENTS ON SLIGHTLY REDUCED RUTILE (TiO_2)

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Several authors have studied the Hall-effect in reduced rutile [1-4], with the current direction both parallel and perpendicular to the c-axis, in the temperature range between 4°K and 700°K. All of these studies were performed, however, on relatively strongly reduced material having resistivities between 0.1 Ω·cm and 50 Ω·cm. Because of the low electron mobility the corresponding carrier concentrations are of the order of 10^{18} or 10^{19} cm^{-3}. One may expect even higher concentrations of the centres (oxygen vacancies or titanium interstitials), from which the electrons are originating. In less reduced samples it has been found that the variation of the specific resistivity, with temperature, T, differs from what is found in strongly reduced crystals [6]. A Hall-effect study of higher resistance material seems therefore of interest, the more so since in strongly reduced material impurity-banding cannot be excluded.

In slightly reduced material a tremendous anisotropy of the conductivity has been reported [5]. In a previous article [6], however, the present authors already demonstrated that the bulk resistivity showed much smaller anisotropy, the anisotropy

being mainly an effect of the resistance of the regions close to the surface. More recently results similar to ours were published by Bogomolov and Shavkunov [7]. The diffusion of oxygen deficiency occurs predominantly along the c-axis [6,8].

Experiments. Rutile single crystals from the National Lead Company, were oriented by Laue-reflections. Samples perpendicular to the c-axis were cut with a diamond saw.

The samples were reduced at temperatures between 500° C and 600° C in a vacuum of 10^{-2} mm Hg. Thereafter they were chemically polished in molten KOH in order to eliminate high resistivity surface regions [9,10]. D. c. measurements of specific resistivity and Hall-constant were made between room and liquid air temperature, on samples having resistivities between 10^2 Ω·cm and 2×10^3 Ω·cm at room temperature. In this region the temperature-coefficient of resistivity changes sign. The corresponding Hall-constants are plotted in fig. 1. The resulting Hall-mobilities are plotted in fig. 2.

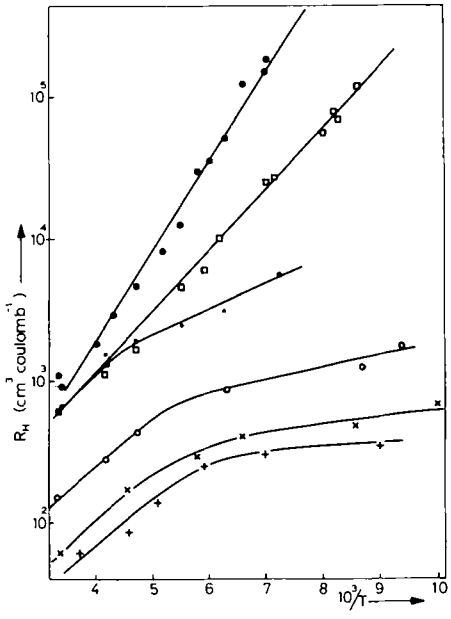

Fig. 1. Hall-coefficient vs. $1/T$.

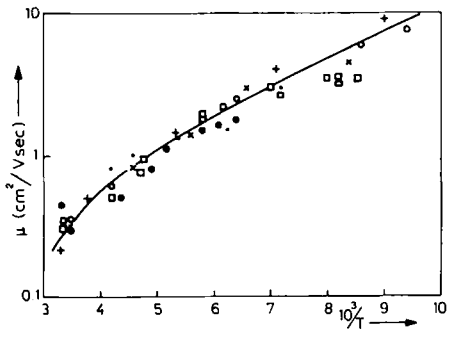

Fig. 2. Mobility vs. $1/T$.

From fig. 1 it is seen that the Hall-constant changes from a complicated behaviour in the 10^2 Ω·cm region to a much simpler behaviour at higher resistivities, where the activation energy found at room temperature equals that at low temperature. It is also found that the mobility data throughout the whole resistivity range correspond well with the mobilities obtained by previous authors [1-4] on material of much lower resistivity. This proves that in our temperature region scattering by donors is negligible. As is seen from fig. 2, at higher donor concentration the Hall-coefficient as a function of reciprocal temperature cannot be described by one activation energy, a fact which was also reported in earlier work on low resistivity material. Measurements [2,3] of the Hall-coefficient down to liquid helium temperatures indicate a maximum at about liquid nitrogen temperature. These complicated phenomena have been interpreted [3] as resulting from the presence of more than one conduction band. Now, however, it is found that at smaller donor concentration the Hall-constant tends to a simpler behaviour with one activation energy only. This suggests that interaction between the donors is a possible reason for the complicated behaviour of the Hall-constant at higher dope. The earlier work [2,3] on strongly reduced material indicates the existence of an activation energy of 10^{-2} eV around 20°K which was interpreted in terms of distance between lowest band edge and donor levels, while the activation energy at room temperature should correspond to the energy difference between the lowest edges of the two conduction bands. While our room temperature activation energy is found to vary with donor concentration and the band-structure is very unlikely to depend on it, this mechanism does not seem probable for our specimens. It is a well-known phenomenon however, that the position of donor levels often depends on their concentration.

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ON THE LOW TEMPERATURE THERMAL EXPANSION OF CERIUM

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Recently, anomalous behaviour in the linear low temperature thermal expansion coefficient α of polycrystalline cerium has been observed [1]. (fig. 1a). The thermal expansion coefficient, being negative for lower temperatures, decreases to large negative values with increasing temperatures. At a temperature of about 12°K, α rises steeply going through zero at 14°K, attaining normal positive values. This anomaly corresponds to the anomalous behaviour observed in the specific heat in the same temperature region [2]*. One attributes this anomaly to a magnetic order-disorder transition occurring at a temperature $T_N = 12°K$ [3].

The purpose of this letter is to give a semi-quantitative description of the thermal expansion coefficient as a function of temperature. At the same time it turns out that it is possible to decide whether the f electron occupies a bound state or a virtual state in Friedel's sense [4].

The volume thermal expansion coefficient $\beta = 3\alpha$ can be expressed in terms of entropy as follows

$$\beta/\chi = (\partial S/\partial V)_T \qquad (1)$$

where χ is the total compressibility and S the total entropy. It is assumed that the total entropy may be separated into a lattice contribution S_g, a conduction electron contribution S_e and a magnetic contribution S_m. Describing the lattice by a Debye model, the conduction electrons by a free electron model,

* For cerium we have used the specific heat curve, obtained after 50 thermocycles. Thermocycling increases the amount of hexagonal phase in a cerium sample. After every thermocycle, the peak in the specific heat curve in the neighbourhood of the transition temperature becomes sharper and larger eventually taking on an asymptotic form. The samples used in [1] contain mainly hexagonal phase. We assume that the specific heat curves for the samples of ref. 1 are almost the same as those of the samples of ref. 3 after many thermocycles.

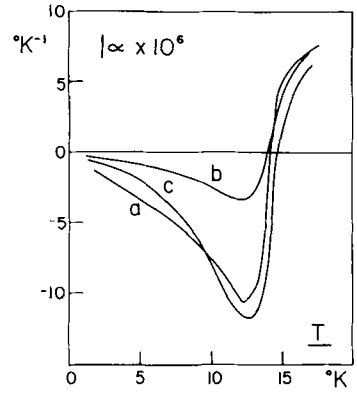

Fig. 1. Linear thermal expansion coefficient of cerium.
a) experimental curve.
b) numerically calculated curve using a bound state.
c) numerically calculated curve using a virtual state.

and assuming that S_m is a function of E_m/T (E_m being the magnetic energy), eq. (1) becomes [5]

$$\beta/\chi = C_g \gamma_g/V + C_m \gamma_m/V \ . \qquad (2)$$

Here C_g and C_m are the lattice specific heat and the magnetic specific heat respectively.
γ_g and $\gamma_m = -(\partial \ln E_m/\partial \ln V)_T$ are Grüneisen constants. In addition it has been assumed that E_m varies very little with temperature, which should be a good approximation above the transition temperature T_N. The conduction electron contribution is small and has been neglected. In order to determine γ_m one has to assume a certain mechanism leading to a magnetic interaction between f electrons on different atoms. Two possibilities will be considered:
a) the f electrons occupy a bound state;
b) the f electrons occupy a virtual state in Friedel's sense.