

Recent developments in solid state magnetism with special reference to transition metal compounds

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Abstract - The magnetic properties of the following transition metal compounds are briefly described: TiH_2 , Fe_3B , MB and M_2B , Fe_2C , Fe_4N , Fe_2P , $Mn(As,Sb)$, $MnBi$, $Co(S,Se)_2$, $Cr(Te,X)$ ($X = ^3Se, Sb$), $TiBe_2$.

INTRODUCTION

Solid state magnetism is one of the most complicated branches of science and technology. It is at the border lines of mathematics, physics, chemistry, metallurgy and materials science, electrical engineering, geology, zoology, medicine, etc. To help with the understanding necessary for further scientific and technological advances this subject must be studied from the broadest possible base using all the theoretical and practical techniques now available. It appears that transition metal compounds form an unusually rich class of materials for such studies and the present talk demonstrates this clearly, apparently for the first time.

The subject has traditionally and unjustifiably been divided into two almost exclusive branches. Fundamental magnetism is concerned with such characteristic properties as the saturation magnetization M and Curie temperature T_c of ferromagnets and the magnetic susceptibility $\chi(T)$ of paramagnets. These have been studied theoretically and experimentally to provide a scientific degree of characterization for both fundamental and applied purposes. Secondary magnetic properties are intimately connected with these primary properties and include such characteristics as the energy loss and coercive force related to the magnetic hysteresis cycle. These latter characteristics are also sensitive to materials properties and thus depend on the metallurgical treatment of the specimens. Both of these types of property have been widely investigated for the sorts of transition metal compounds with which this meeting is concerned. It is proposed to list a series of such compounds in illustration and in the prescribed order and to summarize in each case which particular property is interesting.

SUMMARY OF COMPOUNDS

TiH_2
The magnetic susceptibility of TiH_x (1), (2) begins to develop sharper maxima at $T \approx 300K$ when plotted as a function of the temperature and as x rises from about 1.70 towards 2.00. The original characterization of TiH_2 as antiferromagnetic was found to be wrong as a result of neutron scattering experiments. The accepted interpretation of the sharp peak is that at this temperature the crystal structure of TiH_2 changes from face centred cubic to face centred tetragonal. For the former phase a band structure calculation (3) shows the presence of a Fermi level in a region of very flat energy vs. wave vector dispersions giving a very sharp peak in the curve of the electronic density of states vs. energy; see Fig. 1(3). This peak leads directly to that observed in the susceptibility vs. temperature curve, since the tetragonal distortion inevitably leads to a decrease of the density of states at the Fermi level. Electronic heat data are compatible with this result (2).

Fe_3B
This compound has a very complicated magnetic structure, the same as that of Fe_3P (4) where there are 3 inequivalent Fe-sites. As a result no band structure calculation has yet been performed. However, the compound is important in the study of amorphous alloys since these technologically important magnetic materials have a short range order corresponding to this structure. A rudimentary tight binding band calculation which regards the Fe atoms as lying on a fcc lattice has been performed (5) and shown to explain the variation with B concentration of the Curie temperature T_c of amorphous Fe-B alloys. The alloys have a potential as low loss soft magnetic materials for transformer cores etc. since the overall crystal anisotropy is zero.

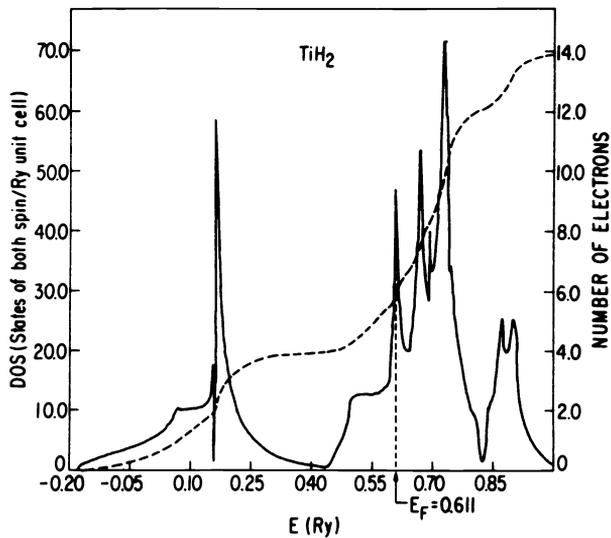


Fig. 1. Electronic density of states curve of TiH_2 (3). Full line, left hand scale; the number of electrons is shown by the dashed line and the right hand scale.

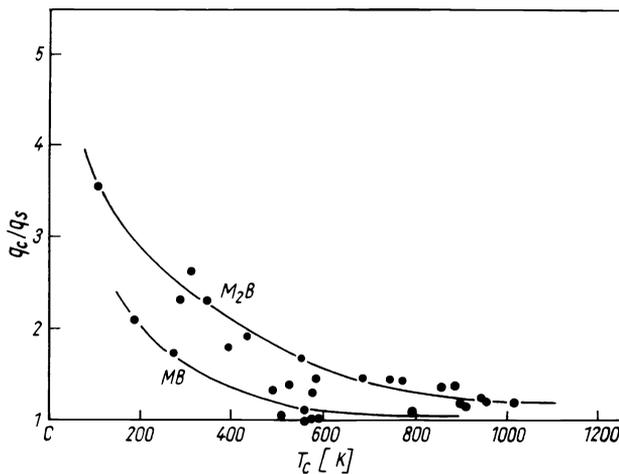


Fig. 2. Ratio q_c/q_s of the magnetic moments obtained from above and below the Curie temperature T_c for a range of transition metal (M) borides (6), (7).

$\text{MB}, \text{M}_2\text{B}$

Magnetic measurements (6), for M = transition elements singly or in two fold combination, show a close correspondence with the corresponding TM alloys. The Slater-Pauling curves (giving the magnetization as a function of composition) are reproduced in form but simply displaced by about 1 atomic species in going from TM alloy $\rightarrow \text{M}_2\text{B} \rightarrow \text{MB}$. This results from an effective charge transfer mechanism. A systematic variation of the ratio of the magnetic moments obtained from measurements above and below T_c is also obtained when plotted against the T_c of the compound itself; see Fig. 2 (6) (7). This variation points to the occurrence of weak "itinerant" or band magnetism.

Fe_2C

What has been called "a relatively rare hexagonal form" of this compound (8) was prepared as a fine powder and was then found to have a relatively high coercive force of at most 800 oersted; the compounds had Curie temperatures T_c about 650K under optimum conditions. These fine particles have permanent magnet potential due to the non-cubic crystal structure leading to large magnetic anisotropies and to the small size giving single domain behaviour. Although Fe_2C has not yet been used in practice this study illustrates that potential technology can be based on fundamental magnetic concepts.

Fe_4N

This compound has been prepared for possible use as a magnetic recording medium (9). For this purpose high coercivity, high saturation magnetization and a high Curie temperature are essential, as is the case for permanent magnet materials. The single domain character was established by electron microscopy of the fine particles produced by nitriding iron particles. The particles were elongated leading to shape anisotropy (maintained during the process) but consisted of a "stereo-network" of small crystallites about 150\AA in size. The coercive forces observed reached about 800 oersted and the saturation magnetization about 145 emu/g if the original iron particles reached about 170 emu/g. Recording characteristics were comparable to those of more standard media.

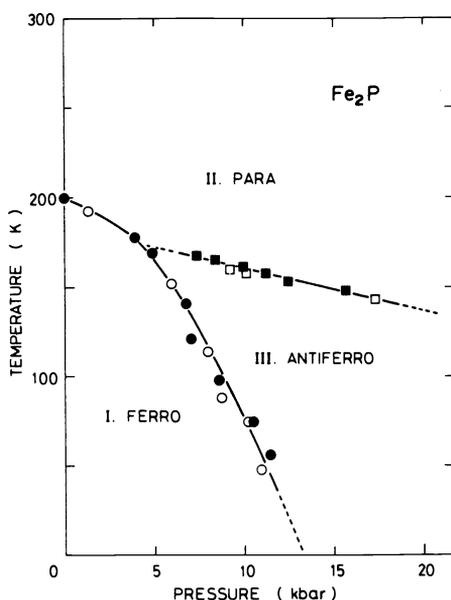


Fig. 3. T,P phase diagram for Fe_2P . Closed symbols, from susceptibility data; open symbols, from resistivity data (11).

Fe_2P

High magnetic field and high pressure measurements on this compound present an unusually rich set of phenomena (10), (11), (12). At zero pressure the low temperature ferromagnetism vanishes at a first order transition to paramagnetism at about 216K. On applying a sufficient pressure Fe_2P (strictly stoichiometric) transforms to an antiferromagnetic state with a triple point at 5 k bar and 170K. Ferromagnetism disappears completely at 13 k bar; see Fig. 3 (11). However, the antiferromagnetic state can be transformed back metamagnetically to the ferromagnetic state in a high magnetic field: At $P = 14$ k bar, $T = 77$ K this field equalled about 6.5 k Oe. All these results point to an unusually interesting energy band structure (13) which it is planned to investigate. In addition Fe_2P is hexagonal and the resulting large anisotropy makes it a potential permanent magnet material.

$\text{Mn}(\text{As};\text{Sb})$

These compounds are almost as interesting as Fe_2P (14). At the As rich end ferromagnetism disappears at a "Curie temperature" in a first order way, $T_C \approx 313$ K for MnAs, the crystal structure changing from hexagonal to orthorhombic. At the Sb rich end and up to 90% As the disappearance of ferromagnetism is second order, T_C for MnSb being 572K with no change of crystal structure. For the whole series of ferromagnetic compounds up to 90% As the pressure dependence of the Curie temperature has been interpreted (14) on the basis of the itinerant electron model giving quantitatively reasonable results. The first order transition for MnAs can no longer be interpreted in terms of a localized model (15) since a band structure calculation (16) gives a consistent picture. For MnAs metamagnetic transitions (17) will thus also have to be interpreted in band structure terms (13).

MnBi

This compound has been prepared in powdered form to produce magnetically hard single domain particles with a large anisotropy arising from the hexagonal crystal structure (for a review, see (18)). Coercive forces up to 12 kOe have been reported. The material has never been produced on a large scale for this purpose. The same goes for MnBi films which at one time seemed most promising for magneto-optic recording using the method of "Curie point writing" (19). There is a surprising lack of scientific data of the type just described for $\text{Mn}(\text{As},\text{Sb})$.

$\text{Co}(\text{S},\text{Se})_2$

These compounds are dichalcogenides with the pyrite structure and exhibit metamagnetic transitions from paramagnetism to ferromagnetism in high magnetic fields up to about 450 kOe for 70% S content (20). The data have been explained in terms of energy band effects (13) (20) making these materials unusually clear examples of itinerant metamagnetism; see Fig. 4 (20).

$\text{Cr}(\text{Te},\text{X})$ ($\text{X}=\text{Se},\text{Sb}$)

These hexagonal materials are ferromagnetic and show interesting properties under high pressures (21). For $\text{X}=\text{Se}$ $dT_C/dp \sim -T_C^{-1}$ as given by itinerant electron theory; T_C vanishes at a critical pressure about 28 k bar. For $\text{X} = \text{Sb}$ $dT_C/dp \sim -T_C$ which is compatible with heterogeneities on an atomic scale (22). High pressure data are thus useful in characterizing metallurgical features of this type.

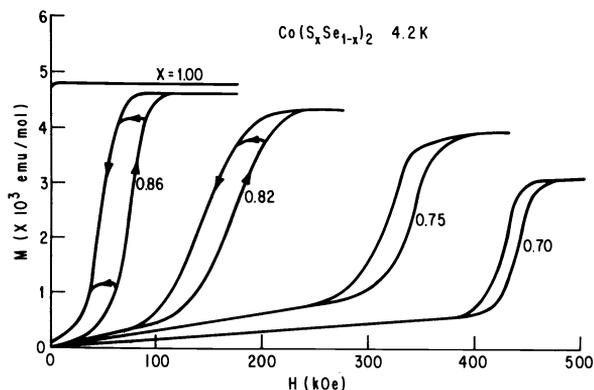


Fig. 4. Itinerant metamagnetism in $\text{Co}(\text{S}_x\text{Se}_{1-x})_2$ (20).

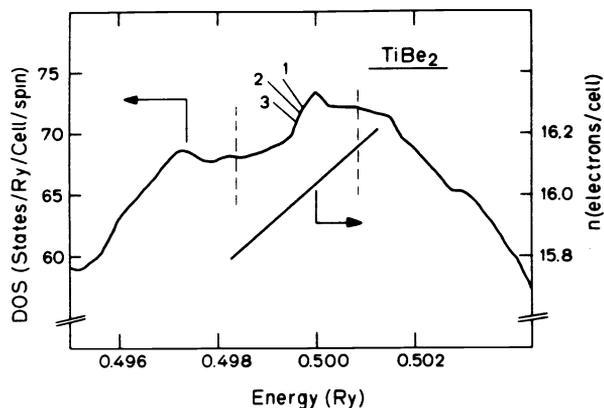


Fig. 5. Electronic density of states curve of TiBe_2 (25). 1, Fermi energy computed; 2, agreement reached with temperature dependence of the paramagnetic susceptibility; 3, agreement reached with field dependence of the susceptibility.

TiBe_2

This Laves phase compound is paramagnetic with a $\chi(T)$ maximum at about 10K. Again this is not evidence for antiferromagnetism! If it is due to the fine structure of the electronic density of states curve (23) the observed but not fully resolved anomalies of the high field magnetization (24) may be correlated both with this phenomenon and with the surprising result that replacing Be by Cu produces an itinerant ferromagnet. Precise band calculations (25) also point to a great sensitivity of magnetism to the band structure; see Fig. 5 (25).

This list of transition metal compounds could be increased many times (MnP, FeGe, Fe₃Si ...). What appears to be of greatest interest is the interplay between the magnetic properties of these materials and their electronic and metallurgical structure.

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