

An Antiferromagnetic to Ferrimagnetic First-Order Phase Transition

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Mn_2Sb is a normally behaving ferrimagnetic compound whose magnetic moment of approximately 0.9 Bohr magneton arises from an antiparallel arrangement of spin moments of manganese ions in two different valence states. For small amounts of certain elements added to Mn_2Sb a first-order phase transition from ferrimagnetic to antiferromagnetic ordering with decreasing temperature occurs at a temperature dependent on the amount of chromium present. This spin ordering transformation is not accompanied by change in crystal structure.

A first-order transformation from ferrimagnetic to antiferromagnetic ordering with decreasing temperature has been reported^{(1), (2)} for $\text{Mn}_{2-x}\text{Cr}_x\text{Sb}$, where $0 < x < 0.2$. In this system the temperature at which the transition takes place is dependent on the amount of chromium present. It has been suggested by Kittel⁽³⁾ that this behavior is due to the appearance of a critical lattice parameter for which the interlattice exchange interaction changes sign. The principal role of the chromium is to introduce a slight contraction in the Mn_2Sb lattice so that this critical parameter becomes accessible during normal thermal contraction. The higher the chromium content, the more contraction is introduced initially and the higher the temperature at which the lattice dimension passes through the critical dimension. In order to make this theory first order, Kittel included the effects of the strain dependence of the isotropic exchange energy.

Several criteria were given to check experimentally the validity of this concept. It was indicated that a discontinuous change in lattice parameter Δa proportional to the square of the sublattice magnetization should occur. Kittel's theory is for a simple array of two equivalent sublattices ordered ferromagnetically or antiferromagnetically. In Mn_2Sb there are two known equivalent manganese sites of moments $\mu_I = 2.13$ and $\mu_{II} = 3.87$ Bohr magnetons.⁽⁴⁾ These sites are ordered in the tetragonal unit cell in such a way that a dense plane of Mn_I has nearest neighbor planes composed of equal amounts of Mn_{II}

and Sb above and below along the direction of the tetragonal axis. This sandwich Mn_{II} - Mn_I - Mn_{II} which is antiferromagnetically ordered has a net moment of approximately 0.9 Bohr magneton per Mn. If the sandwiches are ferromagnetically ordered, we have the Mn_2Sb structure; if the sandwiches are antiferromagnetically ordered, we have the low-temperature $\text{Mn}_{2-x}\text{Cr}_x\text{Sb}$ phase.⁽²⁾ Thus the sublattice of this discussion is the 3-layered set Mn_{II} - Mn_I - Mn_{II} (not the usual sublattices comprised of equivalent sites), and its magnetization is just half of the macroscopic magnetization. Excellent agreement is obtained between Δa and $(M/2)^2$ with a proportionality constant of 10^5 gauss²/Å for transition temperatures ranging from 80°K. to 400°K., the temperature range that we have investigated most thoroughly.

If the principal role of the atom substituting in the Mn_2Sb lattice is to contract the lattice, other modifications of Mn_2Sb should also exhibit a similar magnetic phase transition. In addition, substitution should be possible either for the manganese, as in the case of the chromium substitution, or for the antimony. Ionic or covalent radii are not good criteria to select atoms for substitution since the bonding in Mn_2Sb is extremely complex, and atoms whose radii are smaller than manganese or antimony as measured in one lattice will not necessarily be smaller in the Mn_2Sb lattice. It has been found that the introduction of copper, vanadium, cobalt or zinc, in addition to chromium, into the manganese sites and that introduction of germa-

nium or arsenic into antimony sites will give qualitatively the same first-order magnetic phase transition as observed in $\text{Mn}_{2-x}\text{Cr}_x\text{Sb}$ where $0 < x < 0.2$. Quantitatively, however, the modifying element also appears to affect interatomic coupling parameters. Neutron diffraction results on the chromium modification indicate that chromium substitutes in Mn_I sites but reduces the moment of Mn_{II} , while substitution of arsenic for antimony increases the Mn_I moment. The result in either case is a net reduction of the macroscopic moment below that of Mn_2Sb . The Curie temperature is also reduced in the modified materials.

The most intensive study of the properties of this magnetic transition have been made on the chromium modification. This material seems as close as possible to an ideal structure of two equivalent sublattices either ferromagnetically or antiferromagnetically ordered. For example: (1) The Mn_{II} position in the unit cell is defined only to an arbitrary parameter along the c axis by the space group $P4/nmm$. The measured parameter $Z=0.295$ remains fixed upon going through the transition. (2) There may be a small discontinuous change in the sublattice magnetization at the transition but the inherent uncertainty in the measured magnetic moments tends to mask the effect. In fact, the sublattice moments as measured by neutron diffraction of $\text{Mn}_{1.9}\text{Cr}_{0.1}\text{Sb}$, whose transition is near room temperature, fit exceptionally well to the sublattice moments calculated from a least-squares fit of the two sublattice molecular field equations to the measured macroscopic moment of unmodified Mn_2Sb providing we correct only for the reduction of the Curie temperature and the decrease in the Mn_{II} moments. For this calculation we have used the Brillouin functions $j=1$ and $j=2$ for the two sublattices. For all except the highest chromium-containing samples, the temperature dependence of the macroscopic magnetization in the ferromagnetic region is the same when corrected for Curie temperature

and for the reduction of the saturation magnetization with increase in chromium content. (3) The high resistivity of Mn_2Sb and its modifications (approximately $200 \mu\text{ohm cm}$ at room temperature) is apparently caused entirely by spin-wave scattering. Lattice scattering should make its appearance near absolute zero. We have found that the resistivity extrapolated to absolute zero from 4°K . is of the order of $1 \mu\text{ohm centimeter}$. This result, coupled with the results that the relative positions of the atoms do not change at the transition and that atom substitution does not change the resistivity in the ferromagnetic region from that of unmodified Mn_2Sb , indicates that there are a large number of conduction electrons, probably of the order of 1 per Mn_2Sb , but that these electrons are relatively unaffected by lattice scattering or changes in lattice dimension. The 30% change in resistivity⁵⁾ at the transition must be due entirely to the change in the spin-wave dispersion relations. (4) Magnetocrystalline anisotropy⁵⁾ for the modified Mn_2Sb is quite similar, albeit complex, to unmodified Mn_2Sb . The slight differences can be accounted for qualitatively by the change in the manganese magnetic moments upon introduction of the modifying atom.

These four observations indicate that we are dealing with an almost ideal case of a spin ordering transformation unaffected by the skeletal lattice, except for the strain introduced into it by the magnetic exchange forces. This result is quite unexpected in view of the potentially complex nature of the Mn_2Sb structure.

References

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DISCUSSION

S. IDA: If the exchange interaction between two ferrimagnetic layers passes through zero, we should expect a large field dependent magnetization just below the transition temperature. Was this phenomenon observed?

H. S. JARRETT: There is of course a large field dependent magnetization, which is

manifested as $\partial T_s/\partial H$, the field dependence of the transition temperature. Thus if one observes the magnetization as a function of field strength for a temperature T_1 near, but on the antiferromagnetic side of the transition, the magnetization will be nearly constant until the transition temperature T_s is lowered sufficiently by the field, then an abrupt and rapid increase in magnetization will occur as the transition temperature T_s is depressed below T_1 .

T. OHYAMA: Are there no vacant sites in the lattice?

H. S. JARRETT: We do not believe there are any vacancies in the structure. X-ray density and measured density are in good agreement.

G. DONNAY: Would an X-ray crystallographer, without help from neutron diffractions, have been able to account in some way for the observed first order transition?

H. S. JARRETT: He would have seen discontinuous change in lattice dimensions, and hence would have realized a first order phase change had taken place. He would not have observed a symmetry change, which is another criterion for a first order phase change. Thus we have, as far as I know, the first well-authenticated case of a first order phase change without a crystallographic symmetry change. As you point out the symmetry change that must occur is in the spin ordering.

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Magnetic and Electric Properties of Chalcopyrite

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The magnetic torque, powder susceptibility and their temperature dependences of a natural single crystal of chalcopyrite are measured. The Néel temperature, the direction of antiferromagnetism and two principal susceptibilities, $\chi_{\perp}$ and $\chi_{\parallel}$, are obtained. These results suggest that chalcopyrite is a typical antiferromagnetics.

From results of measurements of conductivity, Hall coefficient, thermoelectric power and photoconductivity it is considered that this material is a semiconductor with a rather large energy band gap.

The crystal structure, the electronic states of constituent elements, magnetic and electric properties are considered together and it is concluded that the 3d-shell in this material is independent of the valence bond which consists of sp^3 bond.

1. Introduction

Chalcopyrite which has a chemical formula, CuFeS_2 , has been known as a semiconductor with its rectifying property. This material is a very interesting semiconductor, since it contains typical magnetic ion, $\text{Fe}^{(+)}$, as a component.

Recently Donnay et al.¹⁾ determined crystal and magnetic structure by neutron diffraction. According to them chalcopyrite was antiferromagnetic at least at room temperature.

The magnetic moment of iron and copper were $3.85 \mu_B$ and $0 \pm 0.2 \mu_B$, respectively.

The ionic state and electric properties of this material were examined by some investigators²⁻⁷⁾. From the consideration of large thermoelectric power and temperature dependence of conductivity they considered that chalcopyrite was an intrinsic semiconductor and the energy band gap was more than 0.5 eV. But there remains some uncertainties about the type of conduction car-