MAGNETIC ORDER AND ENERGETICS OF DIPOLAR COUPLING IN MAGNETIC SUPERCONDUCTORS

Martha Redi and P. W. Anderson*
Princeton University**
Princeton, New Jersey 08544

ABSTRACT

The exact (not just nearest neighbor) dipolar coupling energy densities for the observed structures of the rare earth Chevrel compounds are calculated by the method of Luttinger and Tisza. The dipolar coupling energy density for the most probable spin configuration is comparable to the observed magnetic transition temperature but the most probable ground state is not found experimentally. The discrepancy between the observed magnetic ground state and that predicted from dipole coupling may arise from conduction electron effects or possibly some strong crystal field effect and should be included in any electronic theory of the superconductive state below $T_M$.

* Also at Bell Laboratories, Murray Hill, N. J. 07974

** The work at Princeton University was supported in part by the National Science Foundation Grant No. DMR 78-03015, and in part by the U.S. Office of Naval Research Grant No. N00014-77-C-0711.
MAGNETIC ORDER AND ENERGETICS OF DIPOLAR COUPLING IN MAGNETIC SUPERCONDUCTORS

Martha Redi and P. W. Anderson*
Princeton University**
Princeton, New Jersey 08544

1. Introduction

The antiferromagnetic interaction energy of the rare earth Chevrel compounds is calculated on the basis of simple dipolar coupling. The compounds are of special interest because they are also superconductors and the connection between their superconductive and magnetic properties is the object of much current experimental and theoretical effort. If the antiferromagnetic transition temperature could be accounted for by dipole coupling of the rare earth moments, the connection between superconductive and antiferromagnetic ordering would be simplified. Essentially, different electrons would give rise to the two effects.

In the rare earth Chevrels the magnetic moments are very large, well separated spatially, and with a relatively low density of conduction electrons. Thus it seemed possible that the molecular field model of the transition temperature due only to dipole coupling could make a significant contribution to the stability of the antiferromagnetic phases of the rare earth Chevrels.

The Chevrel compounds are characterized by sulfur cubes filled in alternate layers by $Mo_6$ octahedra or metal, $M_1$, each $M_2$ or $Mo_6$ filled cube separated from the next by an empty sulfur cube; the sulfur cubes themselves forming a BCC lattice. This structure permits the inclusion of a great variety of $M_2$. When $M_2$ is a superconductor, (Sn, Pb), the Chevrel compound is found to be superconducting with raised transition temperature. $T_c$ is increased more for those of lowest $T_{1m}$. If $M_2$ is not superconducting, (Ag, Cu), the Chevrel compound becomes superconducting. If $M_2$ is a rare earth having a large free ion magnetic moment, the Chevrel compounds exhibit both magnetic and superconducting ordering. In particular

---

* Also at Bell Laboratories, Murray Hill, N.J. 07974
** The work at Princeton University was supported in part by the National Science Foundation Grant No. DMR 78-03015, and in part by the U.S. Office of Naval Research Grant No. N00014-77-C-0711
TBMo₆S₈, DyMo₆S₈, and HoMo₆S₈ are found to be superconducting and at lower temperatures to exhibit antiferromagnetic, antiferromagnetic and ferromagnetic order.

II. Method of Luttinger and Tisza

The rare earth atoms lie on a nearly cubic lattice (rhombohedral angle \( \alpha \approx 89.4^\circ \)). The exact mean field dipole coupling interaction energy for an ordered array of moments can be calculated by the group theoretic method of Luttinger and Tisza. A simple cubic dipole array is denoted by placing a dipole of definite moment and direction at every lattice point. The lowest energy ordered arrays are those which are invariant under translations of the form

\[ \Gamma^2 = l_1(2i) + l_2(2j) + l_3(2k), \]

where \( i, j, k \) are integers, \( i, j, k \) are unit vectors in the x,y,z directions. To generate such \( \infty \) arrays we have to specify 8 dipoles, one at each corner of the unit cube. The whole ordered array is constructed by the translations \( \Gamma^2 \). The resulting array may be considered as a superposition of eight \( \infty \) arrays each of which consists of parallel dipoles.

Every array of class \( \Gamma^2 \) can be specified by a set of 24 members, e.g., \( m_i, \) \( i = 1, 2, \ldots, 24 \).

Every set of 24 real numbers defines a \( \Gamma^2 \) array and denotes a point in a 24 dimensional vector space \( R \). Arrays of constant dipole strength form a 16 dimensional hypersurface in \( R \).

To compute the energy of a particular array \( \vec{M} \), it is necessary to know the field generated by \( \vec{M} \) at all the lattice points. The field \( \vec{f} \) of a dipole \( \vec{\mu} \) at a point \( \vec{r} \) is

\[ \vec{f} = \left[ 3(\vec{\mu} \cdot \vec{r}) - \vec{\mu} \right] / r^3, \text{linear in } \mu. \]

The field generated by \( \vec{M} \) will have the same symmetry as the array. The set of vectors representing the field at the lattice points will also correspond to a vector in the space \( R \), and will be denoted by \( \vec{F} \). \( \vec{F} \) may be written \( \vec{F} = F \vec{M} \).

Luttinger and Tisza show that any array of the class \( \Gamma^2 \) may be written as a linear combination of the 24 basic arrays (Fig. 1):

\[ X_i Y_i Z_i \quad i = 1, 2, \ldots, 8. \]

These basic arrays form a complete set of 24 orthogonal vectors.
\[
\mathbf{M} = \sum_{i=1}^{8} (a_i \mathbf{X} + b_i \mathbf{Y} + c_i \mathbf{Z}).
\]

\(\mathbf{X}\) and \(\mathbf{Y}\) are obtained from \(\mathbf{Z}\) through cubic rotations. The field corresponding to \(\mathbf{M}\) is
\[
\mathbf{F} = \sum_{i=1}^{8} (a_i, f_i \mathbf{X} + b_i, f_i \mathbf{Y} + c_i, f_i \mathbf{Z})
\]
and the energy
\[
U = -\frac{1}{2} \sum_{i=1}^{8} (a_i^2 + b_i^2 + c_i^2) f_i
\]
where \(f_i\) is the field at a lattice point due to ordered dipoles in an infinite array \(\mathbf{Z}\). The computation of the energy of any array is reduced to the knowledge of the characteristic values \(f_i\).

The results of numerical computation of \(\{f_i\}\) for the 24 infinite arrays \(\mathbf{X}, \mathbf{Y}, \mathbf{Z}\) from Table II of Luttinger and Tisza in units of \(\mu^2 a^{-3}\):

\[
\begin{align*}
    f_1 &= 0 \\
    f_2 &= -9.687 \\
    f_3 &= 4.844 \\
    f_4 &= 4.844 \\
    f_5 &= 5.351 \\
    f_6 &= -2.676 \\
    f_7 &= -2.676 \\
    f_8 &= 0
\end{align*}
\]

From this table the lowest energy for the simple cubic lattice is \(-f_8/2 = -2.676 \mu^2 a^{-3}\). The corresponding array is \(a_5 \mathbf{X} + b_5 \mathbf{Y} + c_5 \mathbf{Z}\) with \(a_5^2 + b_5^2 + c_5^2 = 1\). If the dipoles were free to rotate they would prefer this ordering with transition temperature \(T_M(Z_5)\) in Table I. A spherical sample is assumed unless otherwise specified.
III. Condensation Energy for Alternating Planes of Parallel Dipoles

The powder neutron diffraction scans of Moncton, et al\textsuperscript{3} for DyMo\textsubscript{6}S\textsubscript{8} and TbMo\textsubscript{6}S\textsubscript{8} below $T_M$ show a simple antiferromagnetic ordering with alternating (100) planes of parallel dipoles, the moments being alternately parallel and antiparallel to a unique direction.

We will assume a temperature independent interaction which constrains the rare earth dipole moments to lie in planes of parallel orientation, the orientation direction being reversed in adjacent planes. We will evaluate the dipolar interaction energy for such an "alternating planar" array having arbitrary dipolar orientation angles $\theta$ and $\phi$.

The $\Gamma^2$ array corresponding to these planes of parallel dipoles is shown in Fig. 2. At lattice points 1, 2, 3, 4, the dipole moment has components

$$m_x = \sin \theta \cos \phi$$
$$m_y = \sin \theta \sin \phi$$
$$m_z = \cos \theta$$

and at 5, 6, 7, 8 components

$$m_x^1 = -\sin \theta \cos \phi = -m_x$$
$$m_y^1 = -\sin \theta \sin \phi = -m_y$$
$$m_z^1 = -\cos \theta = -m_z$$

These are the 24 components of $\vec{M}$.

For arbitrary $\theta, \phi$ in terms of the basic arrays

$$\vec{M} = -m_x X_2 + m_y Y_4 + m_z Z_4$$

and

$$U = -\frac{1}{2} \left[ m_x^2 f_3 + m_y^2 f_4 + m_z^2 f_4 \right]$$

with

$$f_2 = -9.687, \quad f_4 = 4.844, \quad \text{becomes}$$

$$U = -2.422 \left[ 1 - 3 \sin^2 \theta \cos^2 \phi \right]$$

In particular, if $\theta = \frac{\pi}{2}, \phi = 0$, the dipoles are perpendicular to the plane, $U = 4.844 \mu^2/R^3$.
and is strongly repulsive; if \( \theta = 0, \phi = \frac{\pi}{2} \), the dipoles are in the plane, \( U = -2.42 \mu^2/R^3 \), an attractive condensation energy; and if \( \theta = \tan^{-1}\sqrt{2}, \phi = \frac{\pi}{4} \), the dipoles are along \([1, 1, 1]\) and \( U = 0 \).

Computation of the dipole interaction energy for alternating planes of parallel dipoles thus favors alignment in the plane and we would expect this structure on the basis of dipole coupling if the dipoles were constrained in planar arrays. This can be rewritten such that \( U \) depends only on the angle \( \alpha \) between the direction of dipole polarization and the axis normal to the planes.

\[
U = -\frac{1}{2} f_4 [1 - 3 \cos^2 \alpha] \mu^2/R^3.
\]

IV. Estimation of \( T_M \) for Planar Arrays of Dipoles

For any ordered array we can compute \( U^{L+T} \), the energy density. Now \(-2U^{L+T}\) is the energy of orientation of each dipole due to interactions with all the others. Equating this energy to the thermal destabilization by fluctuations in \( \theta, \phi \) directions = \( 2(\frac{1}{2} k_B T_M) \) allows an estimation of the temperature required to destroy the antiferromagnetically ordered state. A negative Luttinger and Tisza energy density corresponds to a magnetic transition temperature

\[
T_M^{L+T} = -2U^{L+T}/k_B
\]

and a \( T_M < 0 \) means the transition is not stabilized by dipole-dipole coupling.

For \( \alpha = \frac{\pi}{2} \), \( T_M \) in Table I have been calculated from

\[
T_M^{L+T} = \frac{1}{k_B} 4.844 \frac{\mu^2}{R^3}.
\]

\( T_M \) are computed transition temperatures for planar arrays of parallel and antiparallel dipoles with dipole orientation in the plane. \( R \) and \( \mu^2 \) used for the estimates were as follows:

The antiferromagnetic temperatures have been calculated with lattice constant \( R = 6.551 \, \text{Å}, \)

the lattice constant for \( \text{PbMo}_4 \text{S}_8 \). The sulfur superstructure provides space for intercalation...
of diverse metal ions and the S-S distance varies very little among the Chevrel compounds. The lattice constants for $M_x = \text{La, Gd, Ho, Er}$ are $6.524, 6.451, 6.449, 6.445\,\text{Å}$. As $Z$ of the rare earth increases, $R$ decreases in the series measured above. Thus $R$ ($PbMo_6S_8$) will cause the estimate of $T_M$ to be too low by about 5%. The lattice constants for $M_x = \text{Dy, Tb}$ are also close to $PbMo_6S_8$.

The antiferromagnetic transition temperatures in Table I have been estimated with $\mu_{\text{free ion}}$, except for $M_x = \text{Tb, Dy, Ho}$ where neutron scattering measurements of $\mu_{\text{neutron}}$ were available. Neutron scattering measures the interaction of the neutron and rare earth magnetic moments whereas susceptibility and transition temperature (condensation energy) involve the square of the rare earth moment. Thus, $\mu_x$, the moment appropriate for calculating $T_M$ and measurable by susceptibility experiments, is related to the neutron scattering moment by $\mu_x = \mu_{\text{neutron}} \sqrt{J+1/3}$. For Tb, Dy and Ho $\mu_{\text{free ion}}$ is less than 10% larger than $\mu_x$.

This calculation would appear to explain the nature of the antiferromagnetic transition in $DyMo_6S_8$ and $TbMo_6S_8$. However, the neutron data show that the dipolar axis is [1, 1, 1]. This structure has zero dipole interaction energy in the simple cubic lattice.

Luttinger and Tisza point out that for nonspherical samples, $-\hbar(4\pi/3-l)N^2\mu^2$ must be added to the energy of the $Z_1$ array. For a long, thin needle $l=0$ and the maximum correction, $-\frac{2\pi}{3} = -2.094$. Any ferromagnetic state will exhibit domain structure optimizing the dipolar energy to this value, and we list the corresponding $T_c$ in Table 2 for Ho. Exchange or other contributions seem to stabilize the ferromagnetic state of $HoMo_6S_8$, since the simple cubic array is always nonferromagnetic, the energy constant of the best nonpolarized SC array being -2.675.

If we calculate corrections to dipole interaction energy for rhombohedral angle = 89.4° we find for $M_5$ and planar, $\alpha = \frac{\pi}{2}$, orientations that $T_M$ changes very little. For the [1, 1, 1] direction of alternately polarized planes of parallel dipoles there is a small attractive interaction of about 4% of that for the most favorable structure.
Some other interaction must stabilize the [1, 1, 1] planar structure. It is not compatible with stabilization by any simple short range exchange interaction.

This calculation then suggests several questions which may be answered by the full microscopic theory of superconductivity for the Chevrel compounds: Why are the dipoles not condensed into \((a_s X_s + b_s Y_s + c_s Z_s)\)? What constrains them to lie in planes of parallel polarization? What determines the direction of polarization to be along [1, 1, 1] and not in the plane? Most puzzling of all, the Table shows that the dipolar energy is just the right order of magnitude to provide the molecular field, and also that except for the direction 111 of magnetization, all of the observed configurations at least are favorable for dipolar interaction, where the antiferromagnetic one is quite implausible as the result of any isotropic exchange interaction.

As Sherlock Holmes said, "When confronted with the impossible, one must accept the implausible." We would almost prefer to believe that the crystal field or some peculiarity of domain structure is misleading us as to the actual observed structure. It is noteworthy that neutron and Mossbauer measurements have given puzzlingly different values for magnetic moment in some similar compounds.

It is quite reasonable that there should be a very strong crystal field effect orienting the dipoles in the 111 direction. To accommodate the unfavorable dipolar field, the state could then be a linear combination of states oriented in 2 or 4 different 111 directions, or some yet more bizarre accommodation. A second implausible possibility is that the induced supercurrents in the Mo₆S₈ groups could be sufficiently strong to contribute appreciably to the dipolar energy or the anisotropy.
References
FIGURE CAPTIONS

Fig. 1: The basic arrays of the class $\Gamma^2$ found by Luttinger and Tisza.

Fig. 2: Coordinate system for calculating the energy of an "alternating planar" $\Gamma^2$ array.
Table I: Experimental and theoretical antiferromagnetic transition temperatures and magnetic moment parameters for the rare earth Chevrel compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_{M}^{OBS}$</th>
<th>J</th>
<th>$\mu_{\text{free ion}}$</th>
<th>$\mu_{\text{Neut}}$</th>
<th>$T_{M}(Z_2)$</th>
<th>$T_{M}$ [planar $\alpha=\pi/2$]</th>
<th>F.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeMo$_6$S$_8$</td>
<td>5/2</td>
<td>2.4$\mu_B$</td>
<td></td>
<td>.10$^0$K</td>
<td>.09$^0$K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pr</td>
<td>4</td>
<td>3.5</td>
<td></td>
<td>.21</td>
<td>.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd</td>
<td>9/2</td>
<td>3.5</td>
<td></td>
<td>.21</td>
<td>.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pm</td>
<td>4</td>
<td>2.7</td>
<td></td>
<td>.15</td>
<td>.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sm</td>
<td>5/2</td>
<td>1.5</td>
<td></td>
<td>.06</td>
<td>.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eu</td>
<td>0</td>
<td>3.4</td>
<td></td>
<td>.21</td>
<td>.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gd</td>
<td>7/2</td>
<td>8.0</td>
<td></td>
<td>1.17</td>
<td>1.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tb</td>
<td>1.0 AF</td>
<td>6</td>
<td>9.5 8.28 8.94</td>
<td>1.44</td>
<td>1.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dy</td>
<td>0.4 AF</td>
<td>15/2</td>
<td>10.6 8.77 9.34</td>
<td>1.61</td>
<td>1.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ho</td>
<td>.64 FM</td>
<td>8</td>
<td>10.4 9.06 9.61</td>
<td>1.66</td>
<td>1.50</td>
<td>1.30</td>
<td></td>
</tr>
<tr>
<td>Er</td>
<td>15/2</td>
<td>9.5</td>
<td></td>
<td>1.64</td>
<td>1.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tm</td>
<td>6</td>
<td>7.3</td>
<td></td>
<td>.97</td>
<td>.88</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yb</td>
<td>7/2</td>
<td>4.5</td>
<td></td>
<td>.35</td>
<td>.32</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Abstract**

The exact (not just nearest neighbor) dipolar coupling energy densities for the observed structures of the rare earth Chevrel compounds are calculated by the method of Luttinger and Tisza. The dipolar coupling energy density for the most probable spin configuration is comparable to the observed magnetic transition temperature but the most probable ground state is not found experimentally. The discrepancy between the observed magnetic ground state and that predicted from dipole coupling may arise from conduction electron effects or possibly some strong crystal field effect and should be included in any electronic theory of the superconductive state below $T_c$. 

**Keywords**

magnetic superconductors