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Eu3P2 AND Eu3As2
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THE FERROMAGNETIC SEMICONDUCTORS Eu₃P₂ AND Eu₃As₂

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Résumé. — Eu₃P₂ et Eu₃As₂ de structure cubique Ba₃P₂ sont ferromagnétiques au-dessus de 25 et 17.5 °K. Leurs propriétés semiconductrices sont démontrées par des mesures de l'absorption optique et de la résistivité électrique.

Abstract. — The Ba₃P₂-type compounds Eu₃P₂ and Eu₃As₂ are ferromagnetic below 25 and 17.5 °K, resp. Optical absorption and electrical resistivity measurements confirm their nonmetallic character.

Today more than a dozen compounds of Eu²⁺ are known to be ferromagnetic at low temperatures. From the viewpoint of structural chemistry divalent europium closely resembles strontium. Valence compounds of Eu²⁺ therefore will be semiconductors as are the corresponding Sr and Ba compounds. Thus, it is not surprising that Eu₃P₂ and Eu₃As₂, besides being ferromagnetic, behave much like Ba₃P₂ and Ba₃As₂, the difference being due to the additional localized f-electrons. Both compounds are indeed semiconductors crystallizing in the bcc Ba₃P₂ structure [1], which is a Gd₄Bi₃ structure, where 1/9 of the anion sites are empty. Each Eu atom is surrounded by 8/9 (3 + 3) anions forming a distorted octahedron. Moreover, each Eu has three Eu neighbours which are closer than in EuO:

<table>
<thead>
<tr>
<th></th>
<th>Eu₃P₂</th>
<th>Eu₃As₂</th>
<th>EuO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu</td>
<td>2.95 A</td>
<td>3.04 A</td>
<td>2.57 A</td>
</tr>
<tr>
<td>Eu—3 (8/9 X)</td>
<td>3.31 A</td>
<td>3.36 A</td>
<td></td>
</tr>
<tr>
<td>Eu</td>
<td>3.54 A</td>
<td>3.62 A</td>
<td>3.64 A</td>
</tr>
<tr>
<td>Eu—2 Eu</td>
<td>3.91 A</td>
<td>3.99 A</td>
<td></td>
</tr>
<tr>
<td>Eu</td>
<td>4.25 A</td>
<td>4.36 A</td>
<td></td>
</tr>
</tbody>
</table>

The magnetic susceptibilities of both compounds obey a Curie-Weiss law with magnetic moments corresponding to the seven noncompensated spins of Eu²⁺. Ferromagnetic ordering takes place below the Curie points of 25 °K (Eu₃P₂) and 17.5 °K (Eu₃As₂), which were determined by specific-heat measurements.

Typical magnetization curves were obtained at 1.6-4.2 °K with pulsed fields of 100 kOe. Within the experimental accuracy the saturation moments agree with the theoretical value for an ⁷S₃/₂ state. Hysteresis-type curves were obtained with samples roughly in the form of toroids using a field coil and a pick-up coil.

The electrical-resistivity behaviour of various bulk samples above 77 °K was typical of impure semiconductors. Reasonable activation energies of the order of 0.5 eV could be derived from the curves only above 600 °K. High contact resistances between the molybdenum leads and the samples prevented measurements with pressed contacts below 77 °K. Resistivity at low temperatures was measured on Eu₃As₂ samples with spot-welded platinum contacts. The resistivity of these samples, which had a very high carrier concentration, revealed a marked peak at the Curie point.

Thin films, 1 000-3 000 Å thick, were prepared on quartz substrates by evaporating bulk material by electron bombardment. Magnetization measurements carried out on Eu₃P₂ films with a torsion balance led to the same Curie point as the bulk material. In Eu₃As₂ films, on the other hand no magnetic saturation was attained with fields up to 13 kOe. Unfortunately, we were not able to measure the electrical resistivity.
of these films in the ferromagnetic range as it exceeded $10^{13} \, \Omega$ (Fig. 2). The optical absorption of these films is shown in figure 3. The absorption edge is near 1.2-1.3 eV.

The low maximum of the optical density below the edge may be due to impurities. At higher energies the absorption curve shows a structure somewhat similar to that of EuTe though less resolved. We therefore assume that the absorption in this energy region is caused by transitions from $4f^7$ states to crystal-field split 5d bands. This interpretation is confirmed by the electron spin polarisation in photoelectric emission, which unequivocally yields the energetic position of the $f$-levels and the impurity states relative to the vacuum level [2].

The red shift of the absorption edge on cooling below the Curie point is much smaller than in the europium chalcogenides but shows qualitatively the same behaviour.

![Optical absorption of Eu$_3$P$_2$ and Eu$_3$As$_2$ films.](image)

**Fig. 3.** Optical absorption of Eu$_3$P$_2$ and Eu$_3$As$_2$ films.

### References
