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1997 J. Phys.: Condens. Matter 9 551

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Electron paramagnetic resonance studies in HgMo_6S_8 doped with Cu^{2+} : evidence for cationic mobility

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Received 10 June 1996

Abstract. Some of the Chevrel phase compounds are reported to exhibit unusual cationic mobilities, particularly those with transition metals. EPR evidence is presented for mobile Cu^{2+} ions in Cu^{2+} -doped HgMo_6S_8 . Evidence is also obtained for the existence of Hg^+ ions, giving possible support for the model correlating the site change with the reaction $\text{A}^{2+} + \text{e}^- \leftrightarrow \text{A}^+$ during ionic conductivity.

1. Introduction

Ternary molybdenum chalcogenides $\text{A}_x\text{Mo}_6\text{S}_8$ (where A is the metal ion and x varies between 1 and 4), termed Chevrel phase compounds, exhibit unusual magnetic and superconducting properties [1]. Among the members of this series, the highest transition temperature ($T_c = 14$ K) and upper critical field ($H_{c2} = 600$ kG) were reported for the PbMo_6S_8 system [2]. In addition, Chevrel phase compounds with a small metal ion, which are rhombohedral at room temperature, undergo a structural phase transition at very low temperatures and high pressures to the triclinic structure. Such lattice instabilities are believed to play an important role in the superconducting behaviour of these compounds [1]. Unusually fast and long-range diffusion of the small cation A has been reported even at ambient temperature in $\text{A}_2\text{Mo}_6\text{S}_8$, where $\text{A} = \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}$ and Cd^{2+} [3–7]. Neutron scattering evidence was obtained recently on $\text{Ni}_2\text{Mo}_6\text{S}_8$ wherein Ni ions were found to be mobile at room temperature [8]. Some of the models that were proposed to explain this unusual phenomenon [6–8] are based on the following suggestions.

- (i) The metal ion has the formal valency A^+ with guest metal–metal bonding, i.e. $[\text{A}–\text{A}]^{2+}$ and dissociation equilibria.
- (ii) The site change during mobility is correlated with the reaction $\text{A}^{2+} + \text{e}^- \leftrightarrow \text{A}^+$.
- (iii) A small ground-state equilibrium concentration of A^{n+} is responsible for the mobility.
- (iv) Small amounts of protons are present and the actual species are $(\text{AH})^+$ ions.

Electron paramagnetic resonance (EPR) of suitable probe ions is highly sensitive to lattice instabilities and mobilities and, therefore, offers a powerful tool for studying these aspects. In the present investigation dealing with the EPR of Cu^{2+} -doped HgMo_6S_8 , evidence is found for mobile Cu^{2+} ions and also for the existence of a low concentration of Hg^+ ions. These observations give support to the $\text{A}^{2+} + \text{e}^- \leftrightarrow \text{A}^+$ model mentioned above.

2. Experimental details

PbMo₆S₈ and HgMo₆S₈:Cu²⁺(0.5%) were prepared by the low-temperature route reported by Tarascon *et al* [9]. The method consists of three steps: preparation of Cu₂Mo₆S₈; preparation of Mo₆S₈ by removing Cu from Cu₂Mo₆S₈; reaction of Mo₆S₈ with low-melting elements Pb and Hg. These compounds were obtained as black powders and are stable in air. The compounds were characterized using the standard x-ray diffraction technique.

In order to understand the electronic and transport properties at microwave frequencies in the normal phase of the compounds, direct microwave absorption experiments (with no field modulation) were conducted using a home-made homodyne bridge consisting of a three-port circulator, a Schottky diode detector, a Varian klystron with a maximum power of 10 mW and a Varian rectangular cavity operating in TE₁₀₄ mode (with unloaded $Q \approx 7000$). The console of a Varian V-4502 spectrometer was used to power the klystron and the detection system. These measurements essentially give changes ΔP in microwave power absorption as a function of temperature. The changes ΔP in power absorption with temperature are measured as changes in the detector current (in microamperes). The microwave power of less than a milliwatt (50–100 μ W) was fed into the cavity which was over-coupled. The power reflected from an over-coupled cavity gives changes in detector current which follows the changes in bulk microwave absorption. At the power level reflected from the cavity and received at the detector, it is expected to be in the square-law region where the change in power absorption is directly proportional to the change in detector current. The sample in the form of a pellet was loaded on a sapphire rod using GE varnish and the temperature was varied from 10 to 300 K using a closed-cycle helium refrigerator (APD cryosystem). The temperature was controlled using a Lake-Shore model 300 auto-tuning temperature controller with an accuracy of ± 0.2 K in this temperature range. For temperature variation in the 300–570 K range, a Varian variable-temperature accessory was used.

3. Results

3.1. Electron paramagnetic resonance of PbMo₆S₈ and Cu²⁺-doped HgMo₆S₈

The EPR of Cu²⁺ in HgMo₆S₈ was studied in the temperature range 10–510 K (normal phase). This is shown in figure 1. A strong isotropic Cu²⁺ signal was observed above 390 K with $g_{iso} = 2.1763 \pm 0.0002$. On lowering the temperature below 390 K, an axially symmetric spectrum of Cu²⁺ with $g_{\perp} = 2.0818 \pm 0.0002$, $g_{\parallel} = 2.4154 \pm 0.0002$, $A_{\parallel} = 132 \pm 2$ G and $A_{\perp} \approx 0$ built up in intensity at the expense of the isotropic spectrum. This happened at and below 245 K. These g -values satisfy the relation $g_{iso} = (g_{\parallel} + 2g_{\perp})/3$ which clearly shows that the high-temperature ‘isotropic’ spectrum is an averaged spectrum of the low-temperature anisotropic spectrum [10]. In figure 1, it may be noted that the ‘parallel components’ (a_1 to a_4) exhibit an m_I dependence of linewidth in the temperature range 10–200 K. In addition to this signal, a sharp EPR signal with $g_{iso} = 2.0036 \pm 0.0002$ and another axially symmetric signal with $g_{\perp} = 1.9391 \pm 0.0022$, $g_{\parallel} = 1.8900 \pm 0.0002$, could also be seen in the figure in the above-mentioned temperature range. The sharp isotropic line, with $g = 2.0036 \pm 0.0002$, was assigned to the even isotope of the Hg⁺ centre ($5d^{10}$, $6s^1$) [11] and the other line with $g_{\parallel} = 1.8900 \pm 0.0002$ and $g_{\perp} = 1.9391 \pm 0.0002$ was assigned to Mo⁵⁺ resonance.

The EPR of PbMo₆S₈ was also recorded for reference and comparison. This is shown in figure 2. In the case of PbMo₆S₈, no EPR signals were observed at room temperature. However, below 150 K, a centre with $g_{\perp} = 1.939 \pm 0.0002$ and $g_{\parallel} = 1.890 \pm 0.0002$

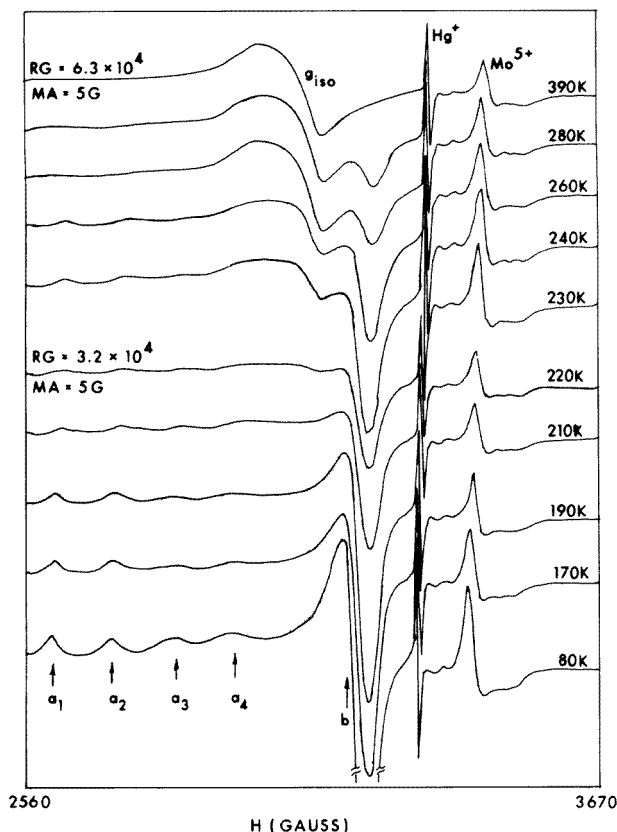


Figure 1. The temperature dependence of the EPR of Cu^{2+} in HgMo_6S_8 in the 390–80 K range. The m_l dependence of linewidths for parallel components (designated as a_1 to a_4) may be noted. The perpendicular component is shown as b . The spectrum at 10 K (not shown in the figure) also exhibits similar features. RG: receiver gain, MA: modulation amplitude.

was seen. The position, shape and width of this signal were found to be temperature independent in the temperature range 10–150 K. Below the superconducting transition temperature $T_c = 14$ K, a weak signal was obtained near zero field. The phase of this signal was found to be opposite to that of the signal at $g_{\perp} = 1.939$. This is shown in figure 3. This low-field signal obtained in PbMo_6S_8 below 14 K is associated with the transition from normal state to superconducting state and had features very similar to that observed in high-temperature superconductors [12, 13] except for its very low intensity.

3.2. Microwave absorption studies on PbMo_6S_8 and Cu^{2+} -doped HgMo_6S_8

Figure 4 gives the changes in microwave absorption as a function of temperature for HgMo_6S_8 doped with Cu^{2+} . The data on PbMo_6S_8 are included for comparison. The increase in microwave absorption with increase in temperature is symptomatic of the metallic character. The $\text{HgMo}_6\text{S}_8:\text{Cu}^{2+}$ compound shows a different behaviour as demonstrated in figure 1. In $\text{HgMo}_6\text{S}_8:\text{Cu}^{2+}$ a steep drop in the microwave absorption was observed at around 245 K. This temperature (245 K) coincides with that at which the EPR of Cu^{2+} has

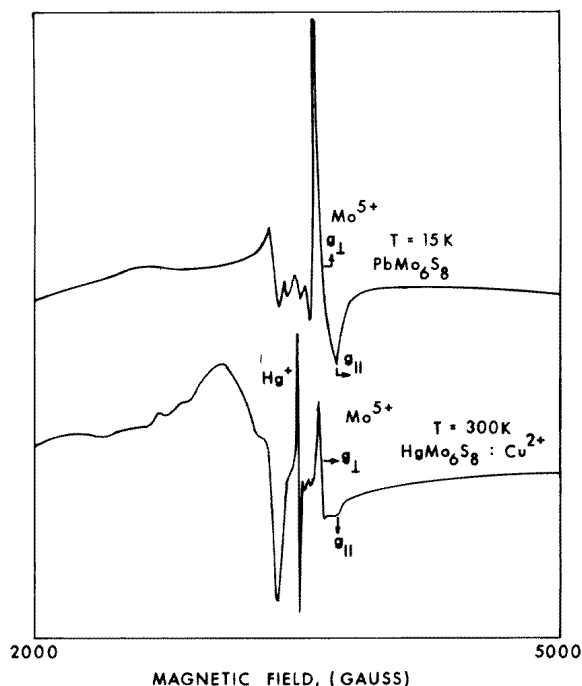


Figure 2. EPR spectra obtained in nominally pure PbMo_6S_8 (at 15 K) and Cu^{2+} -doped HgMo_6S_8 (at 300 K). The EPR signal of Mo^{5+} is seen in both, whereas additional lines due to Hg^{+} and Cu^{2+} (see also figure 1) are observed for HgMo_6S_8 .

shown a transition from an isotropic to an anisotropic spectrum.

4. Discussion

The temperature dependence of the EPR spectrum of Cu^{2+} in HgMo_6S_8 (figure 1) shows that, at high temperature, it consists of a broad isotropic line with an unresolved hyperfine structure. On decrease in the temperature an anisotropic spectrum builds up at the expense of the isotropic spectrum. As mentioned earlier, the relationship between the low- and high-temperature g -values clearly shows that the high-temperature spectrum is the thermally averaged low-temperature spectrum. The EPR of metal ions such as Cu^{2+} and Mn^{2+} was used [14] to monitor the mobility of cations in superionic conductors such as β -sodium gallate and PbF_2 , where the effects of dynamical disorder could be clearly seen. Similarly the present case is clearly due to either a mobile metal ion (Cu^{2+}) or a dynamic \rightarrow static Jahn-Teller effect. The sharp drop in the microwave absorption occurring in the same temperature range suggests sudden changes in the mobility of charge carriers and/or density of charge carriers. In view of the reported mobility of the metal ion at the A site in Chevrel phase compounds and also wide temperature range over which the transition occurred it is more likely that it is a case of mobile Cu^{2+} . The fact that the isotropic g -value corresponds to the average of the anisotropic values means that the copper ion is always in the same environment, i.e. either it exhibits fluxional behaviour at one site (static to dynamic transition) or it is hopping from one site to an equivalent site, the

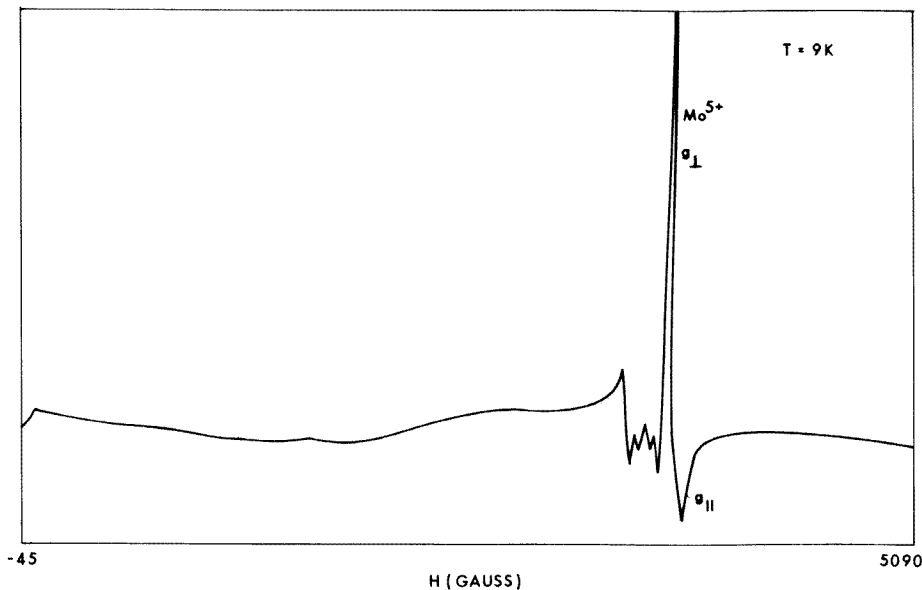


Figure 3. The low-field 'superconductivity' signal in EPR measurements of PbMo_6S_8 at 10 K.

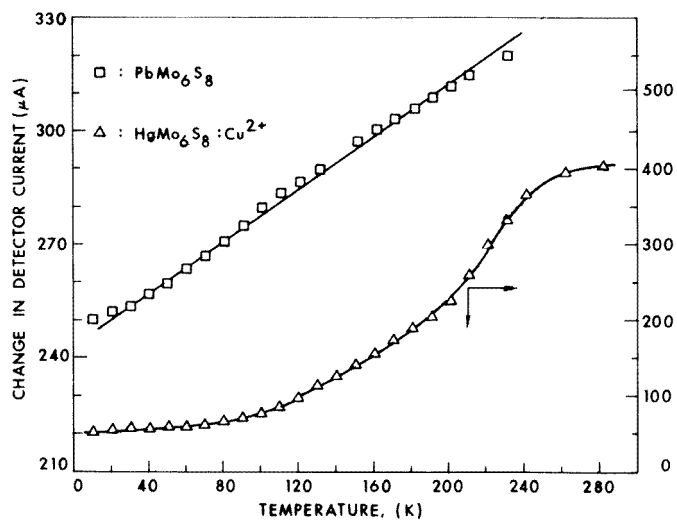


Figure 4. The temperature dependence of direct microwave absorption for PbMo_6S_8 and $\text{HgMo}_6\text{S}_8:\text{Cu}^{2+}$.

hopping time constant being very short compared with the time spent on a site. The microwave experiments favour the second alternative. Even at 20 K the hyperfine structure on the parallel component exhibits an m_I -dependent linewidth. The m_I dependence of linewidths occurs owing to dependence of the spin-lattice relaxation T_1 on the quantum number m_I . This arises whenever random motion resulting in partial or complete averaging of anisotropies contributes to spin relaxation [15]. Therefore, the m_I dependence of the

linewidth in the Z spectrum is a clear symptom of mobility in a preferential direction with the ion hopping between equivalent sites. The low-temperature g -values suggest that the coordination at Cu^{2+} has elongated octahedral symmetry. As mentioned in the introduction, the mobility is likely to be due to one or more of the four mechanisms suggested. In mechanism (ii), the site change during the mobility is correlated with the reaction $\text{A}^{2+} + \text{e}^- \leftrightarrow \text{A}^+$. In the present case, the host lattice A ion is Hg^{2+} and the probe ion in its monovalent state is diamagnetic. Since Hg^+ is paramagnetic, its observation in the present study coupled with the evidence for Cu^{2+} mobility gives considerable support for the $\text{A}^{2+} + \text{e}^- \leftrightarrow \text{A}^+$ model. It may be noted that mobility of Hg^+ cannot be monitored as it has an isotropic g -value. Furthermore, these results do not support the presence of $(\text{AH})^+$ as the spectrum would have shown a clear proton hyperfine structure.

5. Summary

We have obtained direct evidence for cationic mobility in HgMo_6S_8 and also for the existence of a small fraction of Hg ions in the monovalent state. These findings support the $\text{A}^{2+} + \text{e}^- \leftrightarrow \text{A}^+$ process but not the formation of $(\text{AH})^+$ species.

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