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Magnetic resonance in molybdenum spinel-like compounds

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Résumé. — Nous présentons des mesures de la largeur de raie $\Delta H$ de spinelles de molybdène dans les phases para-magnétique et ferromagnétique, effectuées surtout au voisinage de la température critique. Les spectres de résonance magnétique ont été mesurés entre 10 et 300 K à l’aide d’un spectromètre standard en bande X. Nous montrons que les variations de $\Delta H$ avec la température peuvent s’expliquer par la présence d’ions à relaxation rapide. Pour les spinelles « purs » elle s’explique qualitativement dans le cadre des théories actuelles. La substitution de ces spinelles par des ions non magnétiques (C, Si, Ge) modifie le comportement critique et l’origine de cet effet n’est pas encore bien comprise.

Abstract. — Measurements of the magnetic resonance linewidth $\Delta H$ of molybdenum spinels are reported for both paramagnetic and ferromagnetic phases, with particular attention to the region near critical temperature. The magnetic resonance spectra have been measured in the temperature range from 10 K to 300 K with a standard X-band ESR spectrometer. It was shown that the characteristic temperature changes of $\Delta H$ could be due to the influence of fast relaxing ions. For « pure » molybdenum spinels it can be qualitatively described in the frame of existing theories. The substitution of these spinels by nonmagnetic atoms (C, Si, Ge) significantly influences its critical behaviour, and the origin of this effect is not yet clear.

1. Introduction.

The ternary molybdenum chalcogenide $\text{Ga}_{0.5}\text{Mo}_2\text{S}_4$ belongs to a large group of so-called magnetic semiconductors with a spinel (or spinel-like) structure. In this group chromium chalcogenides spinels of type $\text{MCr}_2\text{X}_4$, such as $\text{CdCr}_2\text{Se}_4$ or $\text{CdCr}_2\text{S}_4$, have been extensively studied because of the possibility of a strong interdependence between the electric and magnetic properties of such crystals. The electron configuration of $\text{Cr}^{3+}$ is $[\text{Ar}] (3d)^3$, while in the case of $\text{Mo}^{3+}$ it is $[\text{Kr}] (4d)^3$; therefore, one should expect similarities in the magnetic properties of molybdenum and chromium spinels. The first information on the existence of molybdenum spinel-like compounds $\text{Ga}_{x}\text{Mo}_2\text{S}_4$ ($x = 0.5-0.7$) was given by Barz [1]. Very recently, detailed studies of magnetic and thermal properties of $\text{Ga}_{0.5}\text{Mo}_2\text{S}_4$ have been performed by Shamrai et al. [2] and by Rastogi et al. [3]. It has been reported [2] that $\text{Ga}_{0.5}\text{Mo}_2\text{S}_4$ crystallizes in cubic symmetry (space group $F \bar{4} 3 m$). The gallium atoms are located mostly at $4a$ positions and a small fraction of them at $4c$ positions. From the crystallographic point of view the molybdenum spinels above 42 K have structure similar to that of the $\alpha$- or $\beta$-phases of $\text{Ga}_{0.5}\text{Cr}_2\text{S}_4$ reported by Huguet et al. [4]. At about 42 K the $\text{Ga}_{0.5}\text{Mo}_2\text{S}_4$ compound exhibits a structural phase transition to a rhombohedral phase [2].

The molybdenum spinel is ferromagnetically ordered below Curie temperature ($T_c = 18.5-18.9$ K according to [2] or $T_c = 19.5$ K according to [3]). The nature of the ferromagnetic ordering is not yet clear. Magnetic properties of $\text{Ga}_{0.5}\text{Mo}_2\text{S}_4$, particularly its low ferromagnetic moment, can be explained in the frame of superexchange interactions weakened by vacancies [2] or in the frame of a Stoner-Wohlfarth model of itinerant electron ferromagnetism.

The main purpose of this work is to study the magnetic resonance of three-component molybdenum spinel $\text{Ga}_x\text{Mo}_2\text{S}_4$ as well as of four-component molybdenum spinel $\text{Ga}_{0.5}\text{X}_{0.5}\text{Mo}_2\text{S}_4$ (where $X = \text{C}, \text{Si}, \text{Ge}$) in order to determine the critical behaviour of the magnetic resonance linewidth in these spinels. It also seems interesting to compare the temperature dependence of the magnetic resonance linewidth in molybdenum spinels with that observed in chromium spinels $\text{Ga}_{0.5}\text{Cr}_2\text{S}_4$ [4].
2. Experimental results.

The powder samples of molybdenum spinels have been prepared by the method described in [2]. The Curie temperatures for the investigated compounds have been determined to be equal:

- For \( \text{Ga}_2\text{Mo}_2\text{S}_4 \) \( T_c = 18.9 \text{ K} \)
- For \( \text{Ga}_{0.5}\text{Cr}_{0.5}\text{Mo}_2\text{S}_4 \) \( T_c = 22.5 \text{ K} \)
- For \( \text{Ga}_{0.5}\text{Si}_{0.5}\text{Mo}_2\text{S}_4 \) \( T_c = 19.0 \text{ K} \)
- For \( \text{Ga}_{0.5}\text{Ge}_{0.5}\text{Mo}_2\text{S}_4 \) \( T_c = 25.0 \text{ K} \).

The magnetic resonance spectra have been measured with standard X-band spectrometer in the temperature range from 10 K to 300 K. The observed resonance lines have Lorentzian shape, except for those near the critical points, where the shape becomes slightly asymmetric. For very broad lines the non-zero value of a resonance line intensity of \( H = 0 \) (\( H \) is external magnetic field) has been observed. This effect, as well as the asymmetry of the resonance lines, have several origins:

- the contributions to the EPR linewidth from diagonal \( \chi^D \) and non-diagonal \( \chi^{ij} \) dynamic susceptibilities. The effect of non-diagonal contributions \( \chi^+ \) and \( \chi^- \) (+ and − indicate the direction of rotation of the circular polarization of the microwave field) has been analysed by Benner et al. [5], and it was shown to be important for broad lines and for non-cubic materials; the effect of the magnetic field on the critical fluctuations pointed out by Huguet et al. [4];
- and the contribution from the dispersive part of \( \chi^{ij} \), important for highly conducting materials.

In the case of polycrystalline materials it is practically impossible to separate the different contributions to the deformation of EPR lines. The separation was not carried out because it seems that the above mechanisms have no significant influence on the critical behaviour of EPR linewidth.

The shift of the \( g \)-value from the value \( g \approx 2 \) was insignificantly small for all samples and for all temperatures and has been neglected. The results of resonance linewidth measurements are presented in figures 1 to 4.

3. Discussion.

3.1 RESONANCE IN \( \text{Ga}_2\text{Mo}_2\text{S}_4 \). — The resonance line in \( \text{Ga}_2\text{Mo}_2\text{S}_4 \) (Fig. 1) is relatively narrow and practically independent of temperature except for a critical broadening near \( T_c \). Such behaviour of the resonance linewidth \( \Delta H \) as a function of temperature is characteristic for magnetic systems weakly coupled to the lattice. The lack of linewidth broadening in the high temperature region \( (T \gg T_c) \) indicates the high stoichiometry of the compound \( (x \approx 0.67) \) and results from the lack of « fast relaxing » impurities (such as \( \text{Mo}^{3+} \) or \( \text{Mo}^{4+} \)) in the system.

The behaviour of \( \Delta H \) for \( T < T_c \) is quite satisfactorily described by the theory developed in [6]. The critical broadening of the resonance line for \( T > T_c \) can be described by the relation:

\[
\Delta H = \Delta H_\infty + A(T - T_c)^{-p}
\]

with \( \Delta H_\infty = 1.250 \pm 0.025 \text{ [Oe]} \), \( \Delta H_\infty = \Delta H(T \to \infty) \), \( A = 4.150 \pm 0.250 \text{ [Oe]} \) and critical exponent \( p = 1.5 \pm 0.5 \).

This result should be compared with mode-coupling theory [7-10] which predicts the linewidth of a Heisenberg ferromagnet to increase like \( \chi^{3/4} \) (\( \chi \) is the internal susceptibility) when the Curie temperature is approached from the paramagnetic side. As a result, taking into account susceptibility measurements [2, 3], one should expect a value of \( p \approx 1 \) in the so-called exchange critical region \( (\chi \ll 1) \). The crossover to a region dominated by dipolar interactions is not observable with in experiment probably because of magnetic field suppressing effect [11].

The linewidth beyond the critical region is temperature independent, so one can expect that the linewidth results from the interplay of both dipolar and exchange interactions. The effect of exchange narrowing leads to the following value of the derivative peak-to-peak linewidth in powder (see for example [4]):

\[
\Delta H_{pp} = \frac{4 g^3 \beta^3 s(s + 1) \sum_j (r_{ij})^{-6}}{\sqrt{3} J}
\]

where \( g \) is the \( g \)-factor, \( \beta \)- the Bohr magneton, \( r_{ij} \) is the distance between magnetic \( i \) and \( j \) ions, and \( J \) is the exchange integral between nearest neighbours. Taking the lattice parameters from [2] and estimating the exchange integral in the frame of molecular field theory \( (J = 1.23 \text{ K}) \), the theoretical value of the linewidth is estimated to equal

\[
\Delta H_{pp}^{th} = 1.190 \text{ Oe}.
\]

This result is very near to the value obtained experi-
mentally:

\[ \Delta H_{pp}^{\text{exp}} \approx 1 \, 250 \, \text{Oe}. \]

A change of linewidth near the point of the structural phase transition \( (T \approx 42 \, \text{K}) \) was not observed, probably because they were masked by just starting critical broadening connected with the magnetic phase transition at about 19 K.

### 3.2 Resonance in Ga_{0.5}C_{0.5}Mo_{2}S_{4} and Ga_{0.5}Ge_{0.5}Mo_{2}S_{4} (Fig. 2 and Fig. 3).

The critical behaviour of Ga_{0.5}C_{0.5}Mo_{2}S_{4} and Ga_{0.5}Ge_{0.5}Mo_{2}S_{4} is similar to that observed in Ga_{0.5}Mo_{2}S_{4}. An important difference is observed in the temperature dependence of the linewidth far from the critical region. Temperature broadening of the EPR linewidth is characteristic for the dense paramagnets with fast relaxing impurities.

The role of fast relaxing impurities can be played by ions of the same elements that form the host magnetic system but with another valence. In four-component molybdenum spinels Ga_{0.5}X_{0.5}Mo_{2}S_{4} (X = C, Ge) the vacancies on 4c sites are filled by X^{4+} atoms and for charge compensation, fast relaxing Mo^{2+} ions are expected to exist. A theoretical approach to the problem of impurities in dense paramagnets was first developed by Gulley and Jaccarino [12]. It was shown that the EPR linewidth in such a system may be expressed in the form:

\[ \Delta H = \Delta H_0 + g\beta(\chi_0/\chi_H) \cdot \delta_{\text{in}} \cdot \frac{x}{x^\prime + 1} \]  

where \( x = \delta_{\text{in}}/\delta_{\text{in}}, \) \( \chi_0 \) and \( \chi_H \) are the impurity and bare host susceptibilities, respectively, \( \delta_{\text{in}} \) is single-ion spin-lattice relaxation rate of impurity, and \( \delta_{\text{in}} \) is the impurity to host cross-relaxation rate.

As the parameter \( x \) increases, the bottleneck opens and the lines broaden in proportion to \( \delta_{\text{in}} \). Spin-lattice relaxation of Mo^{2+} is due to the Raman scattering of optical phonons (with the energy \( k\theta \)) localized on impurities [13]. Such effect leads to the following expression for linewidth:

\[ \Delta H = \Delta H_0 + B \exp(-\theta/T) \]  

with
\[ \theta = 180 \, \text{K} \quad \Delta H_0 = 4 \, 620 \, \text{Oe} \]
\[ B = 7.4 \times 10^4 \, \text{Oe} \]  

for Ga_{0.5}C_{0.5}Mo_{2}S_{4} and
\[ \theta = 440 \, \text{K} \quad \Delta H_0 = 5 \, 850 \, \text{Oe} \]
\[ B = 4.4 \times 10^4 \, \text{Oe} \]  

for Ga_{0.5}Ge_{0.5}Mo_{2}S_{4}.

Similar behaviour of the EPR linewidth far from the critical region has been observed by Huguet et al. [4] for chromium spinels Ga_{0.66}Cr_{2}S_{4} (\( \theta = 220 \, \text{K} \) for \( \beta \)-phase of Ga_{0.66}Cr_{2}S_{4}).

### 3.3 Resonance in Ga_{0.5}Si_{0.5}Mo_{2}S_{4}.

The linewidth data for Ga_{0.5}Si_{0.5}Mo_{2}S_{4} in figure 4 shows the characteristic line maximum in both paramagnetic as well as ferromagnetic phases. The linewidth maximum in paramagnetic region may be considered as an example of the crossover in dynamic properties as a function of temperature. Far above the Curie temperature the mode-coupling theory [7-10] predicts a region in which the influence of the dipolar forces on the critical correlations is negligible and the spin-relaxation rate increase as \( \chi^{3/4} \). Close to \( T_c \) a region dominated by dipolar interactions is predicted in which the spin-relaxation rate should decrease as \( \chi^{-1} \).
Above the critical region, a slow decrease of the EPR linewidth with increasing temperature is observed. This effect corresponds to the completely « unbottlenecked » region ($x \gg 1$), where the linewidth is determined by $\delta_{Eg}$ alone (see EPR of RbMnF$_3$ : Fe$^{2+}$ in [12] for comparison).

The peak of the linewidth in the ferromagnetic region has been associated with Mo$^{2+}$ ions which have to be considered as fast relaxing impurities. The effect of fast relaxing impurities on the FMR linewidth is described by the slow relaxation mechanism (see e.g. [14], [15] and references therein) which predicts the occurrence of a maximum in the temperature dependence of the linewidth. The peak in the temperature dependence of $\Delta H$, clearly seen in figure 4, in the case of Ga$_{0.5}$C$_{0.5}$Mo$_2$S$_4$ and Ga$_{0.5}$Ge$_{0.5}$Mo$_2$S$_4$ reaches higher values than in the case of Ga$_{0.5}$Si$_{0.5}$Mo$_2$S$_4$ (and is unobservable).

4. Conclusion.

In conclusion, it has to be stressed that the temperature dependence of the resonance linewidth of molybdenum spinels in both paramagnetic and ferromagnetic phases can be qualitatively described in the framework of existing theories. The substitution of molybdenum spinels by nonmagnetic atoms (C, Si, Ge) significantly influences the critical behaviour of the investigated spinels. The origin of this effect is not yet clear.

References: