SHORT COMMUNICATIONS

DILEMMA OF $EuMo_6X_8$ $(X = S, Se)$ — POSSIBLE SOLUTION

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Amongst Chevrel phase compounds, $REMo_6X_8$, where RE:La, Ce, Pr, Eu, Gd, Lu etc and X:S, Se, Te, $EuMo_6S_8$ and $EuMo_6Se_8$ are of particular interest as both of them show rather unexpected properties which still remain to be understood. From theoretical considerations[1,2] both of them are expected to exhibit superconductivity at ambient pressure with appreciable T_c, which is contrary to the experimental observations. Under a pressure of 7 kbar, however, $Eu_{1.2}Mo_6S_8$ becomes superconducting at about 11 K whereas $Eu_{1.2}Mo_6Se_8$ does not show superconductivity up to pressures of 25 kbar studied[3,4]. The reason for the dilemma is not unambiguously known and the suggested reasons like sharp variation of $N(E_F)^5$, and magnetic to nonmagnetic transitions[6] for Eu ions are not found experimentally true. The ESR studies reported here seem to resolve the dilemma.

Recently, Hambourgar *et al*[7] have tried to relate the pressure induced superconductivity of $Eu_{1.2}Mo_6S_8$ to the possible metal to insulator transition below 110 K, suggested by negative dR/dT of resistance vs temperature plot which is supressed under pressure and they have argued that the metallic state thus retained is the prime cause of superconductivity. This however appears erroneous as Chu *et al*[8] have found that at a much higher pressure of 59 kbar, inspite of the metallic state, $Eu_{1.2}Mo_6S_8$ is no more superconducting. The problem turns all the more baffling when we consider the resistance behaviour of $Eu_{1.2}Mo_6S_8$ and $Eu_{1.2}Mo_6Se_8$. It is interesting (figure 1) that while the former shows negative dR/dT below 110 K (and becomes superconducting under imposed pressure of about 7 kbar) the latter exhibits a rapid drop in resistance around the same temperature (and no superconductivity is observed even under higher pressure). Chu *et al*[3] and Harrison *et al*[5] have unsuccessfully tried to explain the dilemma and more recently Huang *et al*[9] have concluded that the observed data remain inexplicable in terms of either differences in volume, valence and magnetic moment or the existing exotic superconductivity mechanisms.

In this note we report the first comparative ESR study of $Eu_{1.2}Mo_6S_8$ and $Eu_{1.2}Mo_6Se_8$ at different temperatures ranging from 77 K to 300 K which
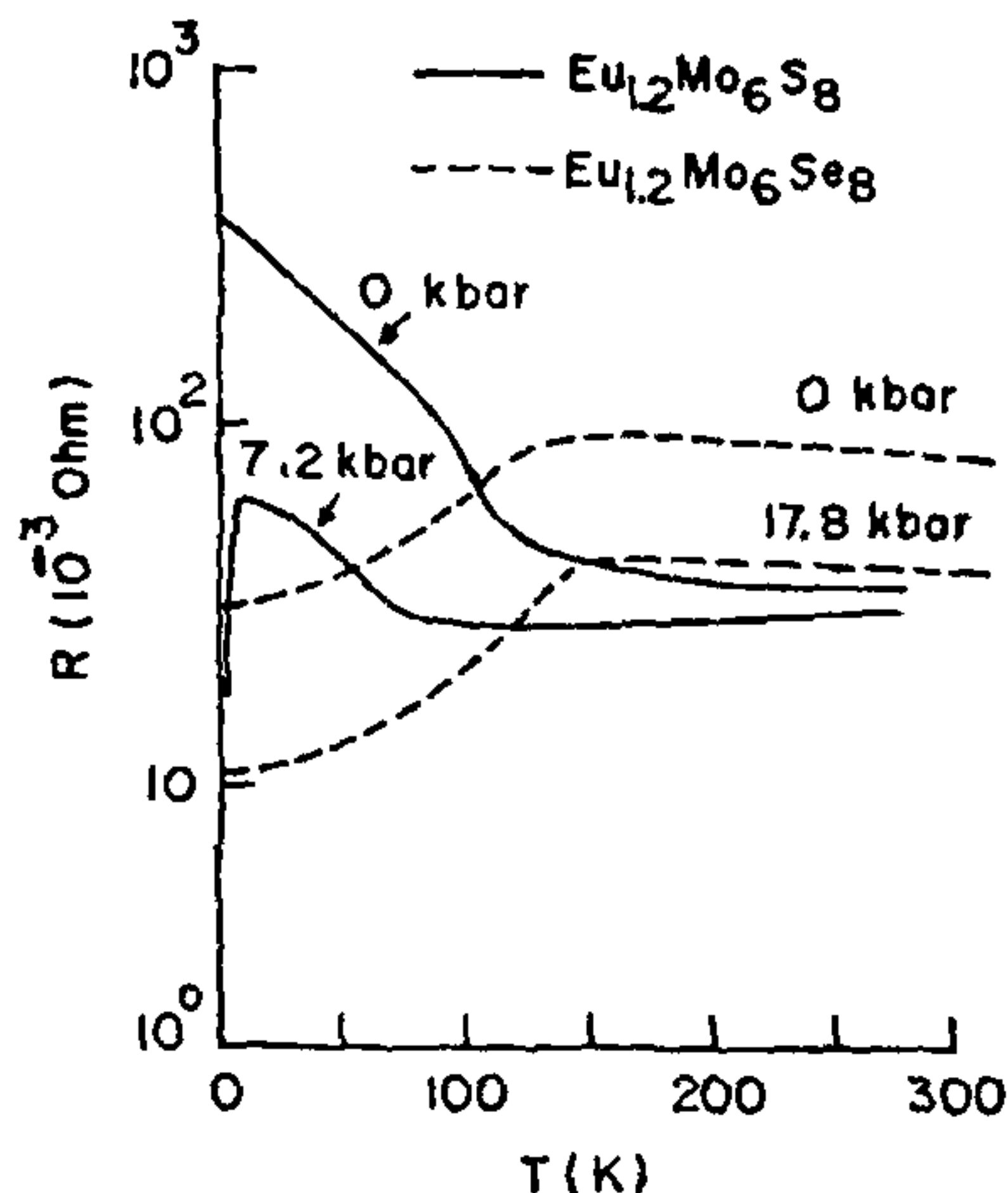
Figure 1. A comparative resistance behaviour with temperature for $Eu_{1.2}Mo_6X_8$ (X:S, Se) with and without imposed pressure.

throws some light on the different resistance behaviours of the two materials. To achieve a more unambiguous analysis we have also studied ESR of Eu^{+2} in $Eu_xPb_{1-x}Mo_6S_8$ containing varying concentrations of Eu.

Figure 2 shows ESR spectra of Eu^{+2} in $Eu_{1.2}Mo_6S_8$ and $Eu_{1.2}Mo_6Se_8$. For both the samples the resonance was a single line with a metalic resonance type[10]. The g and ΔH values are nearly as reported by Peter and Matthias[11] confirming the Eu^{+2} behaviour. The observed g value for the former is 1.95 while for the
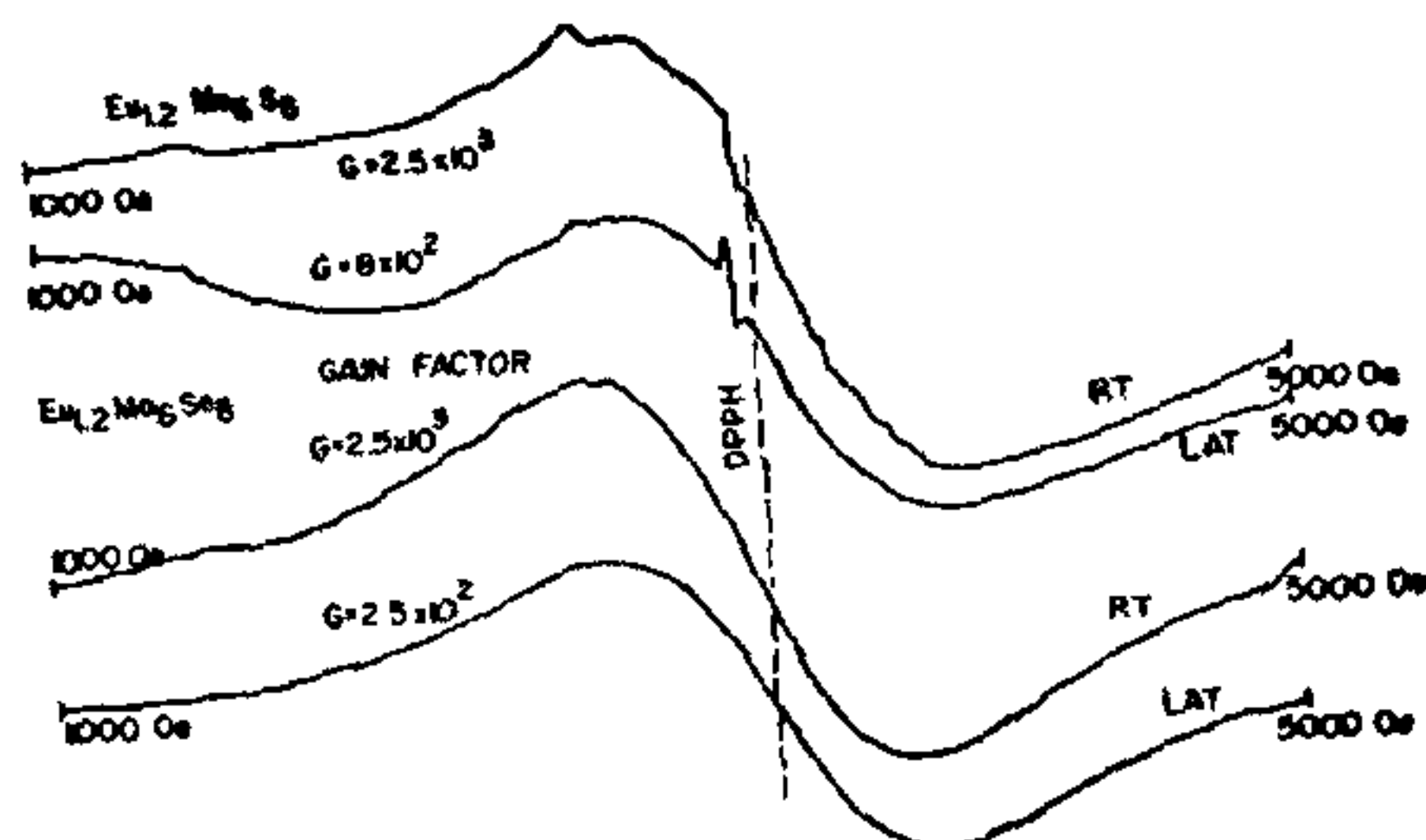

Figure 2. ESR spectra of Eu^{+2} in $Eu_{1.2}Mo_6X_8$ (X:S, Se) at room temperature (RT) and liquid air temperature (LAT).

latter it is 2.00. The line width ΔH for both samples is about 1000 Oe. No change in line width has been found with temperature as in ref. 11. This can be due to the dominance of exchange interactions among conduction electrons or due to the higher concentration of Eu ions. It has also been observed previously in Al:Gd and LaAl$_2$:Gd systems that at higher concentrations of Gd, the line width change with temperature is reduced[12] The exchange coupling parameter J, calculated using the equation $\Delta g = 2(g_1^{-1}) N(E_F) J$[13] (where $g_j = 1.99$) is found to be -0.02 eV and $+0.005$ eV respectively for the above samples at ambient temperature. The polarization of conduction electrons by Eu^{+2} ions is well reported in literature[14,15]. Thus the positive and negative J values clearly show that the exchange coupling between the Eu^{+2} and the conduction electrons is negative in the case of Eu$_{1.2}$Mo$_6$S$_8$ while positive for Eu$_{1.2}$Mo$_6$Se$_8$. This is much expected as in EuMo$_6$S$_8$; the small S framework and the large Mo octahedron make the d-f (antiferromagnetic) interaction to be dominant and in EuMo$_6$Se$_8$ the larger Se framework and smaller Mo octahedron make the s-f (ferromagnetic) interaction to be dominant. This is a major difference in these two apparently very similar materials and as we will see below this is primarily responsible for the observed differences in their transport properties.

The ESR study below 110 K, where there is an onset of negative dR/dT for EuMo$_6$S$_8$, shows that the negative J of Eu$_{1.2}$Mo$_6$S$_8$ has increased nearly by, three folds to —0.06 eV. This is due to the fact that although g remains invarient, heat capacity measurements of Baillif *et al*[16] show that $N(E_F)$, after the crystal structure transformation, is reduced by a factor of one-half. The increase in the negative J is expected to cause Kondo like resistance behaviour which is clearly manifested by negative dR/dT for Eu$_{1.2}$Mo$_6$S$_8$ below 110 K, this has been suggested previously by Maple *et al*[17]. On the other hand in Eu$_{1.2}$Mo$_6$Se$_8$, the J value continues to be positive at lower temperatures which precludes Kondo like behaviour and a sharp decrease in resistance is observed. The resistance drop, $+J$ value and nine fold increase in intensity of ESR line suggest a possible formation of itinerant ferromagnetic state as observed in ZrZn$_2$[18].

It is worth comparing the above data on Eu$_{1.2}$Mo$_6$S$_8$ with Eu doped PbMo$_3$S$_8$ compound where Δg, and hence J are again negative. As shown in figure 3, ΔH of Eu^{+2} is relatively narrow in Eu$_x$Pb$_{1-x}$Mo$_6$S$_8$ with $X = 0.25$ and 0.5, while in Eu$_{1.2}$Mo$_6$S$_8$, ΔH is broader by a factor of almost 100. This suggests that in samples containing smaller concentrations of Eu^{+2}, the solute-solute (*i.e.* Eu^{+2}—Eu^{+2}) interaction is not predominant as observed by Ordermatt[19] and the interaction may
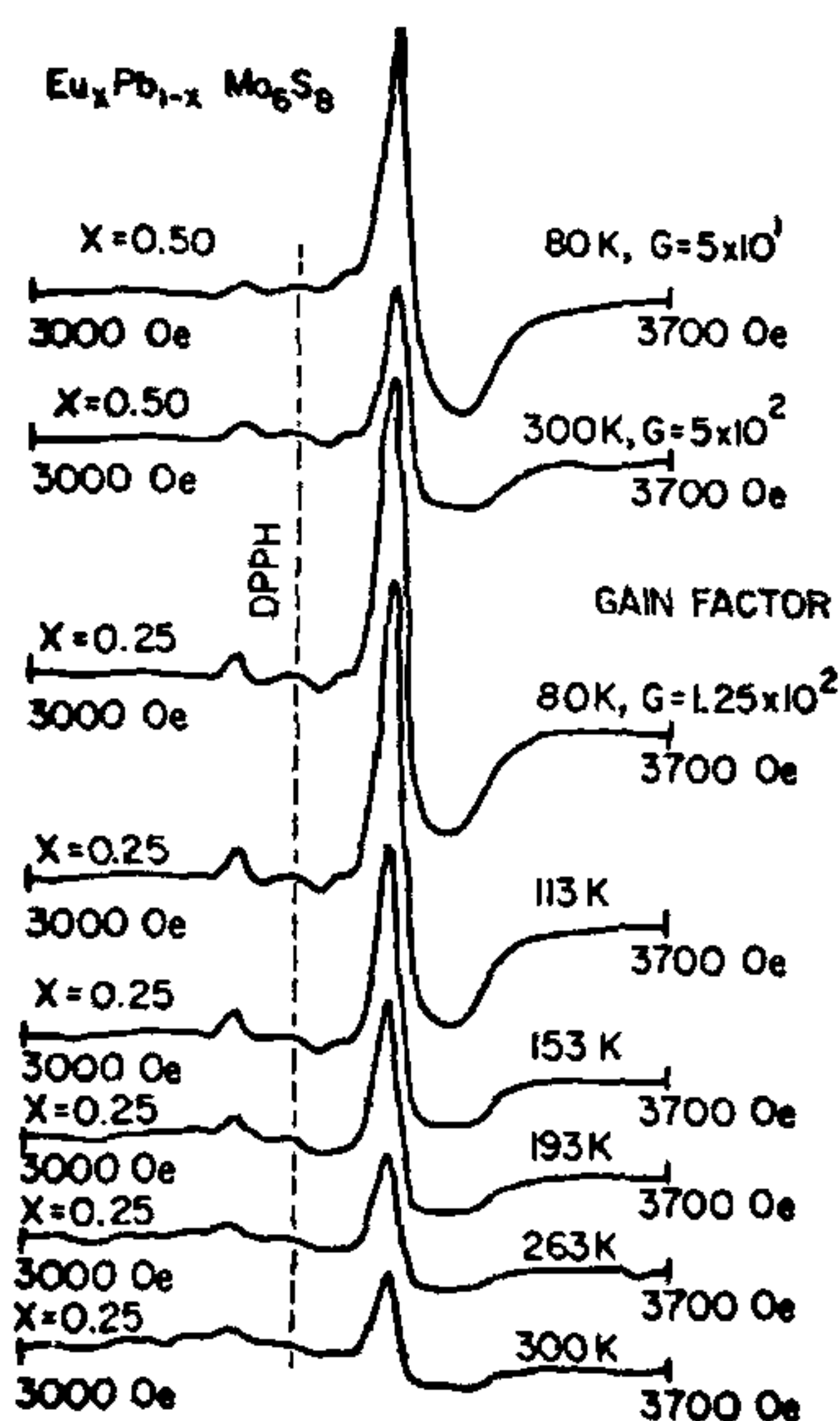

Figure 3. A comparative ESR spectra of Eu^{+2} in Eu$_x$Pb$_{1-x}$Mo$_6$S$_8$ at different temperatures.

be due to the formation of fvbs interacting with conduction band. In Eu rich compounds namely Eu$_{1.2}$Mo$_6$S$_8$ and Eu$_{1.2}$Mo$_6$Se$_8$ the broadening of the line suggests solute-solute interactions, through RKKY[20] mechanism *via* the exchange interaction between conduction electrons and Eu^{+2} ions is dominent. Manifestation of this is the formation of spin glass state in Eu$_{1.2}$Mo$_6$S$_8$ observed at very low temperatures and at ambient pressure[21].

The above study strongly suggests of obvious differences in the EuMo$_6$X$_8$, X:S or Se, which beyond any reasonable doubt seem to account for their different resistance behaviours. This may give a useful clue as to why the former under pressure becomes superconducting while the latter does not.

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CRYSTAL STRUCTURE OF DIAQUA NITRATOGLYCINECALCIUM(II) NITRATE

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GLYCINE forms complexes with many inorganic salts and acids[1,2]. Some of these complexes have therapeutic values and all of these are of chemical and bilogical interest[3,4]. The crystal structures of these simple molecules may serve as model systems in understanding the complicated structures of macromolecules. Hence, a systematic study of the complexes of glycine with many inorganic salts and acids was taken up. The crystal structures of the complexes of glycine with $CaCl_2$,[5,6] $CaBr_2$,[7,8] CaI_2,[9,10] $CdCl_2$,[11] $CdBr_2$[11] and H_3PO_4[12] had earlier been elucidated. In the present study the crystal structure determination of diaquanitratoglycinecalcium(II) nitrate was taken up.

Single crystals of the above complex $(NH_2CH_2COOH)\ Ca(NO_3)_2 \cdot 2H_2O$ were grown from a saturated aqueous solution, containing stoichiometric amounts of glycine and calcium nitrate. The crystal data are as follows: $a = 6.865(5)$, $b = 13.250(10)$, $c = 11.275(6)$ A, $V = 1025.6$ A^3, F.W. $= 275.2$ $D_{mea} = 1.82$ g.cm^{-3}, $D_{cal} = 1.78$ g.cm^{-3}, $Z = 4$, $\mu(CuK\alpha) = 64$ cm^{-1} and the space group is $P2_12_12_1$. The density was measured by flotation method using a mixture of bromoform and carbon tetrachloride.

The three-dimensional intensity data were collected using an Enraf-Nonius CAD-4 diffractometer, with graphite monochromatised CuKα radiation at IIT, Madras. Absorption, Lorentz and polarisation corrections were applied on these 1165 unique reflections for which intensity data were collected. From a three-dimensional Patterson synthesis, the position of the calcium atom was determined.

Thereafter, successive Fourier and difference Fourier syntheses revealed the rest of the structure. Structure-factor least-squares refinement using the block-diagonal approximation was carried out on an IBM 1130 computer. With anisotropic thermal parameters for all the non-hydrogen atoms, the resi-