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Distinct ln$T$-dependent resistance of $Ce_{1.2}Mo_6S_8$ under high pressure

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We have measured the resistivity and ac magnetic susceptibility of $Ce_{1.2}Mo_6S_8$ up to ~120 kbar down to 1.2 K. The antiferromagnetic state is first enhanced and then suppressed by pressure. Meanwhile the resistance becomes to increase logarithmically with decreasing temperature over a large temperature range. The results are discussed in terms of existing models.

Since the $4f$ level of the Ce atoms is close to the Fermi level, the interaction between the otherwise completely localized $4f$ electrons and the conduction electrons is strong. As a result, the Ce atoms can be found in a magnetic, a Kondo, or a nonmagnetic state, depending on the Ce-Ce interaction strength, which is variable by compressing or alloying. The study of the competitions between different magnetic interactions, especially in concentrated magnetic systems,[1–5] has been of great current interest. Unfortunately, the complexity of the phase diagrams and the large phonon contribution to the resistance of the compounds previously investigated make the interpretation difficult. $Ce_{1.2}Mo_6S_8$ (Ce-Mo-S) crystallize in a ternary Chevrel phase[6] in which the Mo clusters form a rhombohedral lattice with open channels to accommodate the Ce atoms in an orderly fashion. In contrast to expectations, Ce-Mo-S is not superconducting. Instead, it has been demonstrated[7] that Ce-Mo-S orders antiferromagnetically at ~2 K and can be treated as a Kondo system. We therefore decided to examine the Ce-Mo-S Chevrel compound under high pressures. As pressure increases, the antiferromagnetic state of the compound has been observed to be first enhanced and then suppressed, and the resistance to become a logarithmically increasing function of decreasing temperature over a wide temperature range. The results will be discussed and compared with predictions of existing models.

We have measured the ac electrical resistance R and the ac magnetic susceptibility χ on eight Ce-Mo-S samples under hydrostatic pressure up to 18 kbar and quasihydrostatic pressure up to 120 kbar between 1.2 and 300 K. The compacted samples were prepared by the sintering technique.[6] The x-ray diffraction pattern showed only a single Chevrel phase with lattice parameters $a = 9.12$ Å and $c = 11.47$ Å in excellent agreement with previously published results.[6] The resolution of our x-ray analyses set a limit of <5% for any second phases, should they exist. Within the resolution of ±10% for the energy dispersion analysis of x-ray, the compositions detected agreed with the nominal values of our samples. The standard four-lead technique was employed for the R measurements and an inductance bridge method for the χ. Both were operated at 23.5 Hz. The hydrostatic environment up to ~18 kbar was provided by a modified high-pressure clamp[8] with the 1:1 n-pentane isoamyl alcohol fluid mixture as the pressure medium. The pressure was determined by a superconducting Pb manometer at low temperature. Compacted sintered samples of dimensions ~$3 \times 1 \times 1$ mm^3 were used for hydrostatic pressure measurements. The quasihydrostatic pressures up to ~120 kbar were generated by using the Bridgman anvil technique[8] with solid steatite as the pressure medium. The applied load, at room temperature, to the anvil set was calibrated against a superconducting Pb manometer in a different run to avoid interference with the R of the samples. Because of the difference in packings from run to run, the quoted quasihydrostatic pressure in this study can be underestimated as much as 15% at 120 kbar. The samples used for these quasihydrostatic measurements were the pulverized sintered compacts of Ce-Mo-S. The sample under pressure was in a disk form with an estimated thickness of 0.01 mm. The resistivity of the samples at 4 K under 120 kbar is estimated to be in the mΩ-cm range.

The temperature dependence of R at ambient pressure previously observed[7] was reproduced in our Ce-Mo-S samples. As shown in Fig. 1, with decreasing temperature, R first decreases monotonically then rises below ~15 K, but with a sharp drop at ~2.5 K. The R minimum at 15 K and the sharp drop at ~2.5 K have been attributed[7] to the Kondo (K) resonance scattering and an antiferromagnetic (AF) ordering, respectively. Under hydrostatic pressures, as shown in the same figure, the room-temperature R decreases rapidly and the low-temperature R rise grows, with only a slight change in the minimum R. At the same time, the temperature T_m for the R minimum is shifted upward, whereas the temperature T_p for the R peak is enhanced initially, but suppressed above ~10 kbar. The low-temperature χ was simultaneously monitored as a function of temperature T at different P's. As displayed in the insert of Fig. 1, the small χ rise, signaling the onset of the AF ordering, increases

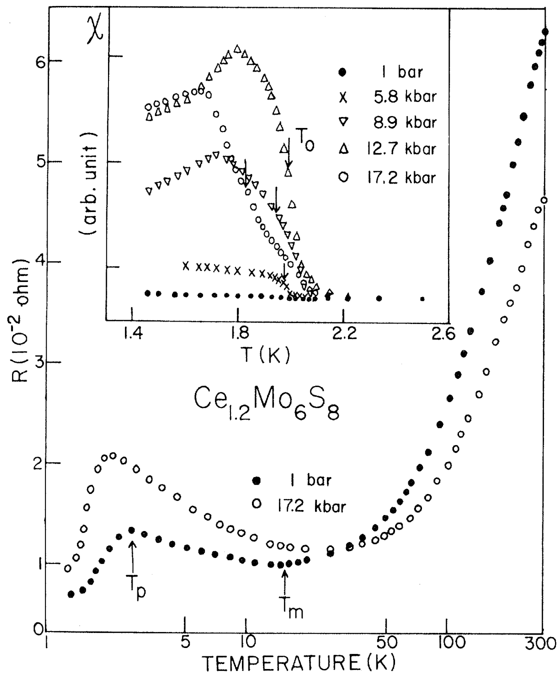

FIG. 1. The T dependence of R and χ of Ce-Mo-S under hydrostatic pressures.

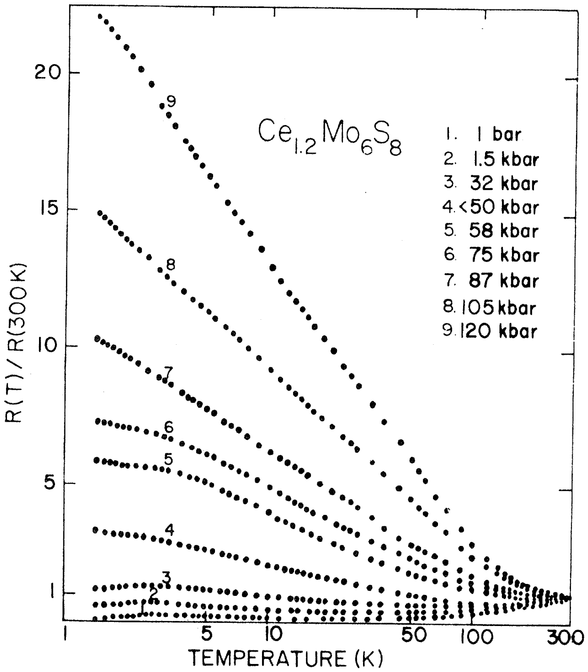

FIG. 2. The T dependence of R under quasihydrostatic pressures except curve 1 which was for a compacted sintered sample determined at atmospheric pressure. Curve 4 was obtained during a P-reduction run.

in magnitude and shifts toward higher P up to ~13 kbar. The reverse is true above ~13 kbar. The above observations are completely reversible on the removal of P. Figure 2 shows the R results normalized to their 300-K values as a function of T under quasihydrostatic pressures. The similar T dependence of curve 1 at 1 bar (obtained with the hydrostatic pressure clamp) and curve 2 at ~1.5 kbar (the minimum P required to establish good electrical contacts of the leads to the sample between the Bridgman anvils) indicates that Ce-Mo-S is not sensitive to the different P conditions in the two high-pressure techniques employed for the present study. As shown in Fig. 2, T_m continues to increase and the low-temperature R rise evolves into a distinct $\ln T$-dependent R over an ever-increasing T range as P increases. Meanwhile, the slope of the R-$\ln T$ plot increases. For example, at ~120 kbar, R increases linearly with decreasing $\ln T$ from 200 down to 4 K, resulting in an ~18-fold increase of R. Curve 4 in Fig. 2, taken after curve 9 on the partial removal of P, demonstrates the reversibility of the P effect on R by use of the Bridgman anvils. Unfortunately, the exact P is difficult to determine during the P-reduction cycle with our experimental arrangement. The R, at 300 K under P, reveals only a smooth monotonic decrease and a small minimum at ~65 kbar when the R minimum in Fig. 1 is shifted to above 300 K.

As mentioned earlier, the R drop and the χ rise in Ce-Mo-S represent a transition to an AF state,[7] consistent with the specific-heat and dc magnetic susceptibility measurements at 1 bar. T_p and T_0 defined in Fig. 1 are therefore a direct measure of the Néel temperature T_N of Ce-Mo-S. As shown in Fig. 3, both T_p and T_0 are initially enhanced and then suppressed by P, forming the phase boundary between a paramagnetic and an antiferromagnetic state. In other words, the AF interaction is a nonmonotonically varying function of P with a peak at ~10 kbar.

It is known that K scattering due to noninteracting magnetic impurity gives[9] rise to a resistance $\propto JN \ln T$, with J being the negative exchange interaction parameter and N the density of states at the Fermi level. The combined effect of this Kondo and the phonon scattering results in an R minimum. The R minimum has therefore been attributed to the K scattering and T_m taken as a qualitative measure of the Kondo temperature T_K. Since T_K is always lower than T_m, the dashed curve in Fig. 3 represents schematically the T_K-P relation. Both T_K and T_m are increasing functions of P up to ~120 kbar. Since T_K is $\propto \exp(1/JN)$, a positive $\partial|JN|/\partial P$ is inferred. The same conclusion can also be drawn from the ever-increasing slope of the R-$\ln T$ plot with P in Fig. 2. This is because $\partial R/\partial \ln T$ is $\propto JN$ due to K scattering.[9] The positive P effect on $|JN|$ can be understood by considering the J which[10] is $\propto |V_{kf}|^2/|E_f - E_F|$, with V_{kf} representing the mixing between the conduction and the $4f$ electrons, E_f the $4f$ level and E_F the Fer-

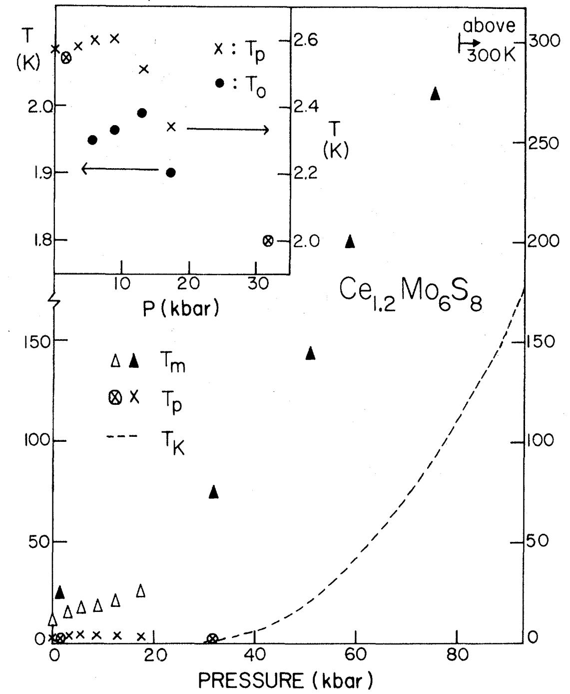

FIG. 3. The P dependence of T_m, T_p, and T_0. Symbols ●, Δ, and × represented runs under hydrostatic pressures and the rest under quasihydrostatic pressures. The dashed curve was drawn schematically to represent the T_K-P relation.

mi level. A positive $\partial|JN|/\partial P$ is then realized either through the increasing mixing between the conduction and $4f$ electrons due to $4f$-band broadening, or through the upward lift of E_f toward E_F by P. Since T_N is $\propto J^2 N$ for an Ruderman-Kittel-Kasuya-Yosida antiferromagnet like Ce-Mo-S, such a positive $\partial|JN|/\partial P$ up to ~120 kbar would also imply a positive $\partial T_N/\partial P$ or $\partial T_0/\partial P$ up to ~120 kbar, in disagreement with our observation. This suggests the possible existence of a competition between various magnetic interactions.

To examine the competition between different magnetic interactions, let us consider the model proposed by Doniach[11] for a concentrated magnetic system called Kondo lattice. According to this model, a transition from an AF to a K state will result when J exceeds a critical value. Calculations made on a one-dimensional analog with one localized spin per cell at 0 K support the proposition, although mathematical difficulty prevents similar calculations from being performed on a three-dimensional system. A qualitative argument for the proposition was also made[11] by comparing the binding energies of the two states. Since they are $\propto \exp(1/JN)$ and $\propto J^2 N$ for the K and AF states, respectively, when $|JN|$ is small, the AF state dominates, while large, the K state prevails. This is in agreement with the phase diagram shown in Fig. 3. The suppression of the AF state by P may therefore be attributed to the interference between the AF and K states, instead to the $4f$ band broadening. Such a band broadening and the ensuing delocalization of the $4f$ moment would have prohibited us from observing the continuous increase in the K scattering after the complete suppression of AF state. Preliminary results on pseudoternary compounds of Ce-La-Mo-S, where J is varied, seem to be consistent with such a model. It should be noted that a similar competition but between a spin-glass and a K state has been previously proposed[12] and observed.[13]

In the above discussion, the $\ln T$ dependence of R has been associated with the K scattering. The unusually rapid suppression of the superconducting transition temperature of the Chevrel ternary La-Mo-S by Ce-Mo-S strongly suggest[7] that Ce-Mo-S can be treated as a Kondo system. The attribution of the low-temperature R rise at 1 bar to K scattering is hence all the more natural. Since the $\ln T$ dependence of R at high P is a continuous outgrowth of such a low-temperature R rise, its association with the K scattering appears reasonable. It should be pointed out that the R considered here is the total resistance of Ce-Mo-S without the subtraction of the background contribution, as ordinarily done for a K system. This may be justifiable in view of the large suppression of R by P above T_m. However, the large T range over which the $\ln T$ dependence is valid, the large R increase with decreasing T, and the lack of indication of an R saturation at low temperature are in strong contrast to expectations[9,14] of a K system. In addition, the model on Kondo lattice is yet to be proved theoretically for a three-dimensional system. Therefore, the possibility of an undetermined type of magnetic excitations responsible for the $\ln T$ dependence cannot be ruled out at the present time. The large resistivity of Ce-Mo-S, approximately a few mΩ cm, at 4 K and 120 kbar is large for magnetic scattering in a metal. Effects on R, the possible creation of a gap[15] as $|J|$ increases, and the localization of defect[16] in Ce-Mo-S under P should also be examined. To investigate some of these possibilities, transport measurements under high pressure in the presence of strong magnetic fields are under way on the Ce-Mo-S and alloyed compounds.

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