Transition of 13-atom, mercury clusters to a strongly paramagnetic state under the action of magnetic field

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Ultradispersed mercury in the form of a cubic lattice comprised of 13-atom clusters was obtained in the cavities of NaA zeolite. As a result of cooling in a magnetic field $H \geqslant 20$ kOe in the 70 to 110-K region, the sample goes to a strongly paramagnetic state ($\chi = 5 \times 10^{-5}$ cm^3/g), which remains at lower temperatures T. Above 110 K this state collapses and $\chi \approx 10^{-5}$ cm^3/g. In the transition region the susceptibility χ oscillates as a function of T and H. A large temperature hysteresis is observed.

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By using zeolites as matrices, it is possible to obtain materials in an ultradispersed state in the form of space lattices comprised of identical clusters containing 10–30 atoms in each zeolite cavity.[1] We obtained a cubic lattice consisting of 13 atomic clusters of mercury in NaA zeolite cavities 11.4 Å in diameter (see Fig. 1), the lattice constant is 24.6 Å. To increase the stability of the samples, we introduced mercury at 20 kbar and ~400 °C for 20 min. Under these conditions we obtained crystals with a density of 3.6–3.8 g/cm^3, which corresponds to approximately 13 mercury atoms in each cavity. The effects described below have been observed only in samples of such density.

Figure 1 shows the dependence of the magnetic moment of the sample $M(T)$, which was obtained after cooling and heating in 15 and 25-kOe fields. In the second

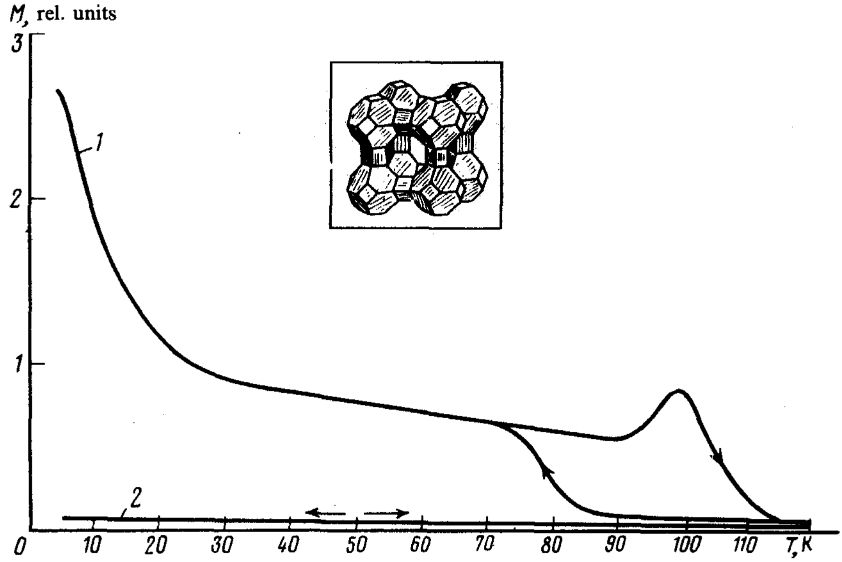

FIG. 1. Temperature dependence $M(T)$ (in relative units) obtained by cooling and heating the sample in a field: 1, 25 kOe; 2, 15 kOe. The unit cell of zeolite NaA is shown in the inset.

case, the magnetic susceptibility in the region of 80 K increases sharply due to cooling and then this state is "frozen" in the sample. At low temperatures the susceptibility is

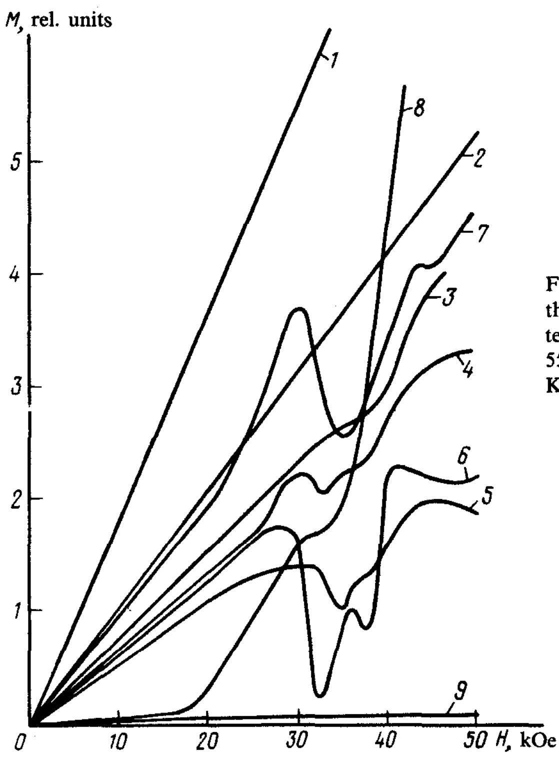

FIG. 2. $M(H)$ dependence (in relative units) of the sample "frozen" in a 43-kOe field as the temperature is increased for: 1, 20 K; 2, 40 K; 3, 55 K; 4, 65 K; 5, 72 K; 6, 80 K; 7, 92 K; 8, 110 K; 9, 125 K.

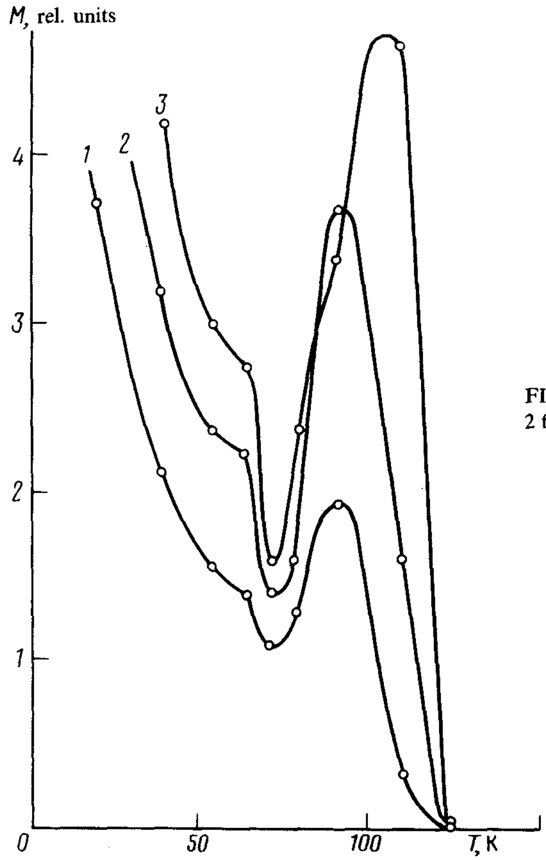

FIG. 3. $M(T)$ dependence from the data of Fig. 2 for the fields: 1, 20 kOe; 2, 30 kOe; 3, 40 kOe.

proportional to $1/T$. A hysteresis is produced as a result of heating, and above 110 K the sample again returns to a weak, paramagnetic state (zeolite and massive mercury are diamagnets). The 70 to 110-K region apparently is the region of super-cooling. Figure 2 shows the $M(H)$ dependence for different temperatures, which was obtained by heating the sample. If this dependence is almost linear at low temperatures, it has a very complex form in the transition region (supercooling). These data are reconstructed in Fig. 3 in the form of the $M(T)$ dependence for different H. It should be noted that the data in Figs. 1 and 3 apparently are not completely equivalent due to the irreversibility of the effects in the region of instability. We can also see that the sample loses the indicated properties after several "freezing-unfreezing" cycles. When the samples are stored, the mercury gradually leaks out of them, which also causes disappearance of the effect.

The magnetic susceptibility is $\chi_{4.2\,K} \approx 10^{-3}$ cm^3/g, which is close to the paramagnetic properties of materials containing iron ions. Both the value of χ and its unusual dependence on the relatively weak magnetic fields and temperature to some extent resemble the situation observed in spin glass; however, the reason for appearance of these properties in a material whose components are diamagnetic is unclear. We can give a number of presumably relevant reasons: 1) the 70 to 110-K region is in that temperature range toward which the melting point of mercury is moving as the size of the sample decreases; moreover, the melting and hardening of such particles is also accompanied by a large hysteresis[2]; 2) the 13-atom cluster has several geometric configurations that are close in energy,[3] which can probably be "unfrozen" at the "melting" point; 3) the effect is tied in to the number of atoms in the 13-atom cluster, which gives 26 electrons, i.e., the same number as that in the iron atoms.

If the Hg_{13} cluster is considered a quasi atom, then, in contrast to the normal atom, in addition to a larger size the field of the cluster's "nucleus" does not have a central symmetry. The peculiarities of the metallic bond remain in particles of such small size.[1]

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