Critical phenomena in EuO

A. S. Borukhovich, M. S. Marunya, V. G. Bamburov, N. I. Ignat'eva, and P. V. Gel'd

Institute of Chemistry, Urals Scientific Center, USSR Academy of Sciences

(Submitted November 25, 1974)
Zh. Eksp. Teor. Fiz. 69, 565–571 (August 1975)

We investigate the specific heat, the magnetic susceptibility, and the magnetization of europium-monoxide compounds with various compositions in the region of the magnetic phase transition. A correlation is established between the thermodynamic parameters of the second-order transition of EuO_{1+x} samples and their magnetic characteristics. The results are discussed under the assumption that the monoxide with oxygen deficit contains bound magnetic polarons, the presence of which is responsible for the metal–insulator transition. This circumstance, and also the contribution of the dipole-dipole interaction, can be the cause of the asymmetry of the $C_p(T)$ polytherm in the critical region.

PACS numbers: 75.30.Jy, 75.30.Cr

Europium monoxide EuO_{1+x}, which has interesting ferrodielectric properties, is homogeneous in a relatively narrow range of compositions ($x = \pm 0.035$).[1] With changing value and sign of x, its conductivity varies in a very wide range, from that typical of metals to that characteristic of insulators. Moreover, samples with definite concentration of O-vacancies undergo, at temperatures somewhat below critical, a metal—insulator temperature transition different from the known Mott transitions.[2] The jump in the conductivity of such samples can reach 13 orders of magnitude.[3]

To explain the nature of this phenomenon, an He-like model[3] or the model of bound magnetic polaron (BMP)[4] were used in a number of studies[3,4] of the paramagnetic characteristics of EuO_{1+x} samples. These models differ mainly only in the definition of the spin orientation of the europium orbital electrons localized near the O-vacancy. It is shown in these papers that the metal-insulator transition occurs only in europium-monoxide compounds that have a slight excess of the metal ($-0.005 < x < 0$), whereas in the case of a large oxygen deficit metallic conductivity is observed in the entire range of investigated temperatures.[5] At $x > 0$ the EuO_{1+x} samples have semiconductor conductivity (with a forbidden band 1—3 eV wide). It was observed also that, unlike the latter, compounds with vacancies in the oxygen sublattice are characterized by an increased paramagnetic Curie temperature, whereas the Weiss constant $C_M = \chi(T - \Theta)$ is not very sensitive to the degree of completeness of the crystal lattice of the monoxide.

EXPERIMENTAL RESULTS AND DISCUSSION

We investigated the temperature dependences of the magnetic and thermodynamic parameters of europium monoxide samples in the region of their magnetic phase transition, for the purpose of ascertaining the details of the influence of the sample composition on this transition. A combined method[6] was used to synthesize europium monoxide compounds with various compositions. According to chemical, x-ray diffraction, and pycnometric analyses, all the samples were single-phase. The compositions of the samples were established by the method of oxidation with the "Thermoflex" instrument of the "Rigaku-Denki" firm.1) The results are given in the table. It was found that compound No. 3 was almost equi-atomic, whereas compound No. 1 contained a slight excess of oxygen while No. 2 had an excess (0.3 at.%) of europium.

At room temperature all samples had low conductivity (from 10^{-6} to $10^{-8}\ \Omega^{-1}\ cm^{-1}$). The magnetic measurements were performed by the Faraday method with a magnetic balance of the Dominicali type. The sensitivity of the setup was $\sim 10^{-8}$ emu/g. The temperature pickup was a copper-constantan thermocouple, and the temperature of the sample was maintained automatically with the aid of a VRT-2 regulator, thereby ensuring the necessary temperature stability (drift not more than 0.05 deg/hr).

The results of the investigation of the temperature dependences of the magnetic susceptibility and magnetization are shown in Figs. 1 and 2. It follows from the experimental data that the paramagnetic Curie temperature varies with the sample composition and is maximal for compound No. 2, which contains vacancies in the oxygen sublattice. The Weiss constant turned out to be the same for all the investigated samples and close in value (C_M = (7.73 ± 0.03 emu-°K/mole) to that established in[4], or 1.8% less than the theoretical value 7.78

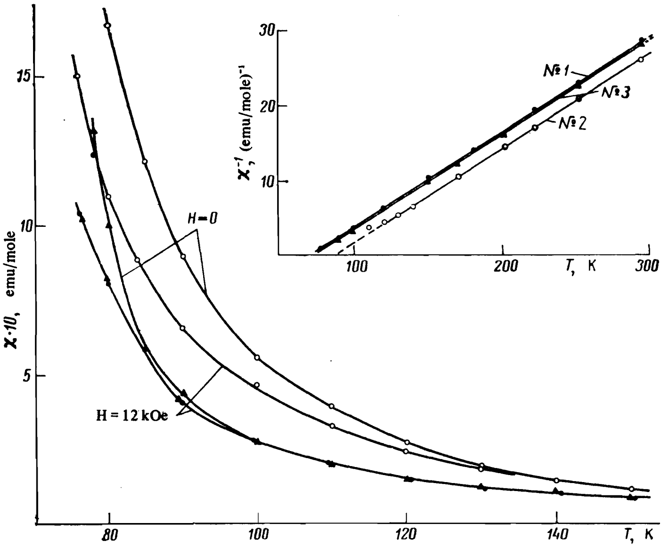

FIG. 1. Polytherms of the magnetic susceptibility χ of samples with different compositions (the curves are labeled with the numbers of the compounds).

for EuO. This result indicates that the samples used in this study were of sufficiently high quality and, in particular, had no segregated Eu_3O_4 impurities.

The results of the study of the magnetization (Fig. 2) indicate that for the stoichiometric compound (No. 3), at $T > T_C$, the magnetization decreases quite rapidly with rising temperature. At the same time for sample No. 2 ($EuO_{0.997}$) the residual magnetization is preserved in a much larger interval of temperatures (up to 130–140°K).

The specific heats of the compounds were investigated at temperatures from 55 to 90°K (up to 300°K in the case of sample No. 2). The temperature pickup (the measurements were made with an adiabatic calorimeter) was in this case a TSPN-2 platinum resistance thermometer, and the temperature regime of the calorimeter and of the adiabatic screen was maintained automatically with accuracy $\sim 2 \times 10^{-4}$ deg. The error in the determination of C_p did not exceed 0.3%. The investigations have shown that the Curie temperature determined from the position of the peak of the specific heat depends quite weakly on the compositions of the investigated samples (Fig. 3). The same result follows also from a study of the influence of the temperature on the magnetic susceptibility of these compounds.

The main singularity of the polytherms $C_p(T)$ obtained by us is the rather distinct correlation between the height and sharpness of the λ peaks and the composition of the monoxide. The most smeared phase transition occured in sample No. 2, whereas the peaks on the $C_p(T)$ plots of samples 1 and 3 turned out to be much sharper. The latter is obviously due to the difference between the jumps of the specific heats of the compounds in the course of their magnetic disordering. To the extent that the EuO_{1+x} samples were synthesized under identical technological conditions, the jump of the specific heat at the Curie point can equally well serve as a characteristic of the compound as does the paramagnetic Curie temperature.

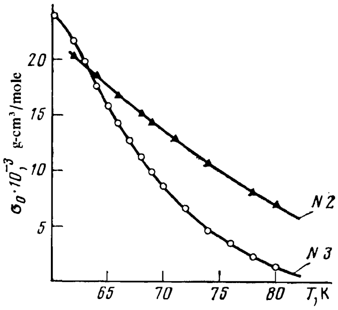

FIG. 2. Effect of temperature on the magnetization σ of the compounds in the magnetic-disorder region.

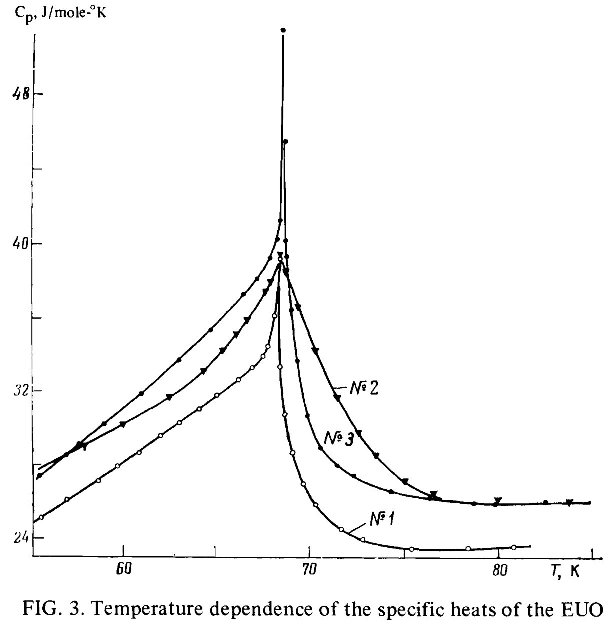

FIG. 3. Temperature dependence of the specific heats of the EuO_{1+x} samples.

The value of ΔC_p was estimated under the assumption that the specific heat has a logarithmic divergence at the Curie point (i.e., the critical exponent of the specific heat is $\alpha \equiv 0$). It follows from our results for samples 2 and 3 that this holds true satisfactorily in the interval $10^{-3} > \tau > 10^{-4}$, where $\tau \equiv (T - T_C)/T_C$; the specific heat in the vicinity of the λ point can be described by the polynomial

$$C_{p\pm} = A_\pm \ln|\tau| \pm B_\pm. \qquad (1)$$

Then the jump of the specific heat, according to[7], is determined by the difference $\Delta C_p = C_{p-}(\tau) - C_{p+}(\tau)$ as $\tau \to 0$.

The values of ΔC_p obtained with the aid of these relations for the investigated compounds are given in the table. As seen from these data, sample No. 2 ($EuO_{0.997}$) has not only a higher value of Θ, but a specific-heat jump that is smaller by one order of magnitude (compared with compounds No. 1 and No. 3). Since both parameters are characterized at $T \geq T_C$ by the fluctuations of the magnetization (or by the magnetic-order parameter[8]), their values should be determined under these conditions by the degree of destruction of the spin correlation, which, according to the results, changes with the composition of the samples. Attention is also called to the fact that a noticeable difference between Θ and T_C is observed for compound No. 2. This difference indicates that short-range magnetic order is preserved in a rather wide temperature range. The same is also evidenced by the noticeable field dependence of the magnetic susceptibility of the given sample, which is observed up to 140°K, whereas for the compounds No. 1 and No. 3 it is confined to a relatively narrow interval (up to 90–95°K) (Fig. 1).

Among the causes contributing to preservation of the short-range magnetic order (the presence of uncontrollable impurities, inhomogeneous distribution of the vacancies, etc.), the most interesting in this case is apparently the existence of magnetopolaron states at the sites of the O-vacancies. Their appearance in ferrodielectrics was deduced mainly from the results of investigations of magnetic and optical characteristics.[9] On the other hand, questions of the influence of the polaron states on the thermodynamic parameters of magnetic semiconductors have hardly been discussed before, even though they are undoubtedly of interest. This pertains, in particular, to the singularities in the behavior of the characteristics in the critical region of the λ point. In this connection, the calculation of ΔC_p made above within the framework of the molecular field theory (MFT) is not quite correct, although in the case of compounds 1 and 3 it leads to values that do not differ greatly from the theoretical estimates (at $s = 7/2$), namely

$$\Delta C_p = \frac{5}{2} Nk \frac{(2s+1)^2 - 1}{(2s+1)^2 + 1} \approx 20 \text{ J/mole·°K} \qquad (2)$$

The approximate character of the estimates obtained in the MFT approximation for europium monochalcogenides is evidenced also by the critical behavior of their magnetic parameters. Thus, the magnetization of EuS in the region of the magnetic transition is characterized by an exponent close to $\beta_+ = 0.33$,[10] as against $\beta_+ = 0.385$[11] (or $\beta_+ = 0.34$[12]) for EuO. The critical exponent for the magnetic susceptibility of europium monoxide, determined from magneto-optical data,[13] turned out to be $\gamma_+ = 1.29$. On the other hand, the study of the specific heat in the critical region[14] has also lead to nonzero exponents that characterize Eq. (1), where it turned out that $\alpha_- \neq \alpha_+$ (i.e., the λ peak has no symmetry).

The foregoing data, however, are difficult to compare with one another, because they describe properties of EuO$_{1+x}$ compounds of different composition (and source). On the other hand, our results have made it possible to estimate the critical exponents for europium monoxide samples of different degree of non-stoichiometry, and without the restrictions imposed by any particular theory. To this end we carried out a computer reduction[2] of the experimental data, aimed at a self-consistent determination of the parameters that characterize the relation

$$f(\tau, n) = A_\pm |\tau|^{-n} + B_\pm. \qquad (3)$$

As is customary in such a case, the values of n and of the coefficients A and B were determined by minimizing the rms deviation

$$\varepsilon = \int |f^{\exp} - f^{\text{appr}}|^2 dT$$

in a specified temperature region by a direct search method. The final result turns out to be stable to the choice of the initial values and to the sequence of variation of the variables.

It has turned out as a result that for all the EuO$_{1+x}$ samples investigated in this study there is no exact logarithmic divergence of C_p near the Curie point. The branches of the polytherms $C_p(T)$ in the critical region for the compounds No. 1 and No. 3 are the most symmetrical (see the table). The latter concerns both the closeness of the values of the exponents $\alpha_\pm$ and the ratio of the coefficients A_+/A_- from (3). For the abovementioned samples it is equal to 1.0 and 1.2, i.e., it satisfies the requirements of similarity theory for second-order phase transition (if the logarithmic divergence of the specific heat is realized).[15] Under the same conditions, the critical exponent β_+ for the magnetization of EuO$_{1.001}$ turned out to be equal exactly to 1/3, and for the paramagnetic susceptibility the corresponding value was $\gamma_+ = 1.15$. These data show that the similarity relations are satisfied in the limit for the critical exponents of stoichiometric europium monoxide, inasmuch as $\alpha_+ + 2\beta_+ + \gamma_+ = 1.97 \pm 0.05$.

Certified characteristics and critical parameters of europium monoxide samples

Sample No.	EuO$_{1\pm x}$	a, Å	Θ, K	T_c, K	ΔC_p (±0.05) J/mole-°K	$\alpha_\mp$ (±0.01)	$A_\mp$ (±0.1) дж J/mole-°K	β_+ (±0,02)	γ_+ (±0.02)
1	EuO$_{1,005}$	5.144	71	68.3	6.5	0.10 0,17	4.4 4.4	–	–
2	EuO$_{0,997}$	5.141	85	68.4	0.8	0.09 0.30	3.6 1,8	0.48	1.36
3	EuO$_{1,001}$	5.146	73	68,5	8.5	0.20 0.16	3.6 2.9	0.33	1.15

The smearing of the λ point of the compound No. 2 (EuO$_{0.987}$) gives rise, as is seen from the table, not only to a noticeable difference between the critical exponents α_- and α_+, as well as to a small value of the ratio A_+/A_- (equal to 0.5), but also points to appreciable deviations from the requirements of the theory of the symmetry of second-order phase transitions. If, however, we take into consideration the value of the exponents β_+ and γ_+ given in the table, then it turns out that in the latter case, too, a relation exists between the critical exponents, but in the form of the strong inequality $\alpha_1 + 2\beta_+ + \gamma_+ > 2$.

Thus, the presented results indicate that the O-vacancies in europium monoxide exert a strong influence not only on its magnetic parameters, but also on its thermodynamic parameters (especially in the region $T \gtrsim T_C$). This result seems to correspond to the conclusions of[14], in which the obtained difference between the exponents α_- and α_+ was attributed to the possible manifestation of a contribution of magnetic dipole-dipole interaction superimposed in the critical region on a direct exchange of the Heisenberg type. According to estimates[16] made for EuS and EuO, temperature intervals in which such contributions cross are observed near T_C (at $10^{-3} < \tau < 10^{-2}$). It can be concluded from this that in this case the manifestation of such a contribution can be attributed to the existence of magnetopolaron states due to the O-vacancies in the EuO$_{1-x}$.

---

[1] The author is grateful to V. A. Zhilyaev for performing the analysis.

[2] We are indebted to L. A. Mokhracheva for the computer reduction.

1. M. W. Shafer, J. B. Torrance, and T. Penney, J. Phys. Chem. Solids **33**, 2251 (1972).
2. S. Methfessel and D. C. Mattis, transl. in: Magnitnye poluprovodniki (Magnetic Semiconductors), Mir, 1972, Chaps. 6 and 7.
3. M. R. Oliver, J. O. Dimmock, A. L. McWhorter, and T. B. Reed, Phys. Rev. 5B, 1078 (1972).
4. J. B. Torrance, M. W. Shafer, and T. R. McGuire, Phys. Rev. Lett. **29**, 1168 (1972).
5. O. Massenet, Y. Capimont, and Nguen Van Dang, J. Appl. Phys. **45**, 3593 (1974).
6. N. I. Ignat'eva and V. G. Bamburov, Neorganicheskie materialy **6**, 154 (1970).
7. A. V. Voronel' and S. R. Garber, Zh. Eksp. Teor. Fiz. **52**, 1464 (1967) [Sov. Phys.-JETP **25**, 970 (1967)].
8. S. V. Vonsovskiĭ, Magnetizm (Magnetism), Nauka, 1971, Chap. 18.
9. M. I. Darby and K. N. Taylor, Physics of Rare Earth Solids, Chapman and Hall, Chap. 6.
10. P. Heller and G. Benedek, Phys. Rev. Lett. **14**, 71 (1965).
11. J. Hog and J. Johansson, Int. J. Magnetism **4**, 11 (1973).
12. G. Groll, Z. Phys. **243**, 60 (1971).
13. C. C. Huang, R. S. Pindak, and J. T. Ho, Solid State Comm. **14**, 559 (1974).
14. M. B. Salamon, Solid State Comm. **13**, 1741 (1973).
15. M. Fisher, transl. in Ustoĭchivost' i fazovye perekhody (Stability and Phase Transitions), Mir, 1973.
16. M. E. Fisher and A. Aharony, Phys. Rev. Lett. **30**, 559 (1973).

Translated by J. G. Adashko
60