New magnetic ground state excited in $EuCrO_3$, by optical pumping

E. I. Golovenchits, V. A. Sanina, and T. A. Shaplygina

A. F. Ioffe Physicotechnical Institute, Academy of Sciences, USSR

(Submitted 1 August 1980; resubmitted 22 December 1980)
Zh. Eksp. Teor. Fiz. **80**, 1911–1925 (May 1981)

A new magnetically ordered ground state in $EuCrO_3$, excited by high-power optical pumping, has been observed experimentally. It is shown that the occurrence of the new state is dependent on exchange interaction between the Eu^{3+} ions, which become magnetic as a result of the pumping, via ions of the Cr matrix ($4f$-$3d$-$4f$ exchange). An investigation of the new ground state of $EuCrO_3$ has been carried out.

PACS numbers: 75.30.Et, 75.50.Dd

A previous paper[1] reported experimental observation of a new magnetic ground state in $EuCrO_3$, occurring as a result of optical pumping. The same paper offered an explanation of the effect with a coupled-exchange-polaron model. But the experiment described there provided the only substantiation of the proposed model. In order to demonstrate the correctness of our understanding of the phenomenon, it was necessary to conduct additional experiments.

The present paper presents the results of magnetic measurements, and also new data on the investigation of antiferromagnetic resonance (AFMR). It studies in detail the formation kinetics and the nature of the new magnetic ground state.

1. PRINCIPAL EXPERIMENTAL RESULTS OF AFMR INVESTIGATION

The resonance measurements were made on an AFMR spectrometer[2] over the wavelength range 0.5–2 mm and the temperature range 4.5–100 K; the cryostat used differed from that described earlier[2] only by the fact that a third window in its lower part made optical pumping possible. The path of the beams of pumping and of millimeter-range radiation is shown in Fig. 1. The specimen holder consisted of two corundum prisms, pressed together tightly but without optical contact; to the lower of them the specimen was fastened, in the form of a plate of dimensions $2\times2\times(1-0.1)$ mm. The specimen was surrounded by a diaphragm, of a material that absorbed well in the millimeter-wavelength range. This construction made it possible to produce the electrodynamic conditions necessary for obtaining narrow AFMR lines and to insure good heat withdrawal from the specimen. The heating of the specimen during the pumping process was monitored with a carbon resistance thermometer and a thermocouple placed near the specimen; and at helium temperatures, under conditions of maximum pumping, it did not exceed 1 K. At high temperatures ($T > 40$ K), however, the overheating of the specimen increased to several degrees.[1)]

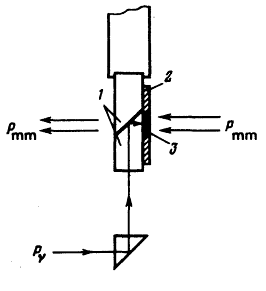

FIG. 1. Schematic drawing of the specimen holder and of the path of the beams of optical pumping and of millimeter radiation. 1) corundom prisms; 2) diagram; 3) specimen.

Optical pumping was accomplished with a pulsed laser LTI PCh-8, at wavelength 532 nm. The maximum power during a pulse was $P_p \approx 280$ kW. The laser beam was slightly focused to spot diameter ~1.5–2 mm. But the position of the spot on the surface of the specimen varied somewhat from pulse to pulse. This led to the result that under prolonged (~100 sec) pumping, the whole surface of the specimen was apparently illuminated uniformly.

The AFMR investigations were made in magnetic fields up to 10 kOe; the field was oriented along the c axis of the crystal. The magnetic structure of $EuCrO_3$ is $\Gamma_4(G_xF_z)$.[3] Both branches of AFMR, transverse (ω_{xy}) and longitudinal (ω_z), were observed. The difference of the activation frequencies ω_{xy}^0 and ω_z^0 for $EuCrO_3$ from the corresponding frequencies in $YCrO_3$[4] is practically completely explained by the difference of the Néel temperatures for these crystals.

In optical pumping, beginning with a certain threshold pumping power and with sufficient duration of the pumping, a new resonance-absorption signal was observed. This signal was shifted with respect to the original AFMR (before pumping) for ω_{xy} toward larger fields (Fig. 2a), and for ω_z toward smaller (Fig. 3). After discontinuance of the pumping, the signal persisted for many hours.

The original AFMR signal either disappeared completely after pumping at maximum power (Figs. 2a and 3), or greatly decreased its intensity and shifted somewhat (Fig. 1 of Ref. 1). Figure 2b shows the variation with field of the frequencies of the original and of the new AFMR signals for both branches.

As is seen from Figs. 2 and 3, during the first few minutes after the shutting off of the laser there was observed a comparatively fast increase of the intensity of the new signal and a shift of it with respect to field

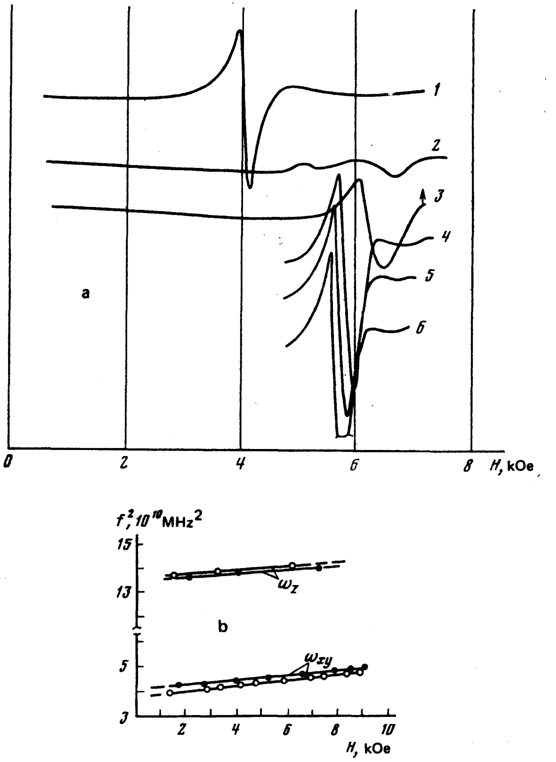

FIG. 2. a) Records of AFMR lines (ω_{xy}) in $EuCrO_3$. Along the ordinate axis Y is the signal intensity. Specimen $2\times1.5\times0.15$ mm, $T=25$ K, $f=210$ GHz. 1) AFMR lines before pumping; 2, 3), at the time of pumping (the arrow indicates the instant of turing off of the laser); 4–6) records of the lines at 2-minute intervals after turing off of the laser. Pumping parameters: power in the pulse $P_p=250$ kW, pulse duration $\tau_p=15$ ns, repetition frequency $\Omega=25$ Hz, duration of pumping $t_{\text{pump}}=2$ min. b) Dependence of the frequencies of the original and of the new AFMR signals on the field for the branches ω_{xy} and ω_z.

(fast relaxation). Later on, the intensity of the signal became practically constant, while the shift of the resonance field slowed up and then also ceased to change. The new resonance-absorption signal existed as long as the low temperature was maintained.

Figure 4 shows the temperature dependences of the resonance fields of the original and of the new AFMR signals. It is seen that beginning with $T\approx90$ K, the signals fuse (in the case of ω_{xy}). In the case of longitudinal resonance, this fusion was not observed because of the sharp increase of the resonance fields with temperature. The pumping was done at low temperatures: $T=25$ K (Fig. 2), $T=5$ K (Fig. 3 and Fig. 2 of Ref. 1). The effect occurred if the temperature at which the pumping was done did not exceed 50 K. Then the crystal heated to 300 K. On subsequent cooling, only the original AFMR was revived. Thus the effect exists only in the low-temperature region. One is struck by the fact that the $H_{\text{res}}(T)$ relation for the new signal in Fig. 4 is similar to the $H_{\text{res}}(T)$ relation in $ErCrO_3$,[2] in which the Er^{3+} ion is magnetic in the ground state. The temperature range in which the effect was observed also coincides with the characteristic temperature range, for rare-earth orthoferrites, orthochromites, and garnets, in which the magnetic properties of the $4f$ ions manifest themselves.

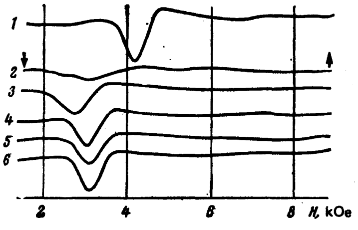

FIG. 3. Same as in Fig. 2, but for AFMR of the type ω_z. Specimen $2\times1.5\times0.115$ mm, $f=372$ GHz; lines 3–6 recorded at 2-minute intervals after turning off of the laser. The arrows indicate the instants of turning on and of turning off of the laser.

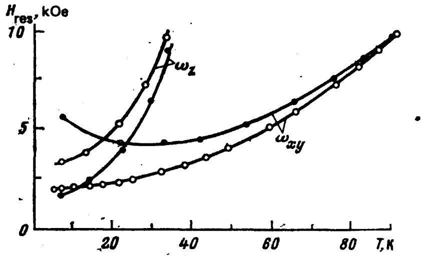

FIG. 4. Temperature dependence of resonance fields H_{res} for both types of resonance (ω_{xy} and ω_z) in $EuCrO_3$. Dark points, AFMR after pumping; light points, AFMR before pumping.

The appearance of the new resonance signal, as it depends on the pumping power, has threshold character. For prolonged illumination but small power in the pulse, the effect did not occur. The signal appeared only beginning with a certain power in the pulse (Fig. 5).

But in the case of pumping with pulses of the maximum power (Fig. 6), with increase of the time of illumination the original signal broadened and dropped in intensity; and beginning with a certain time (~40 sec), a new signal appeared, whose intensity increased

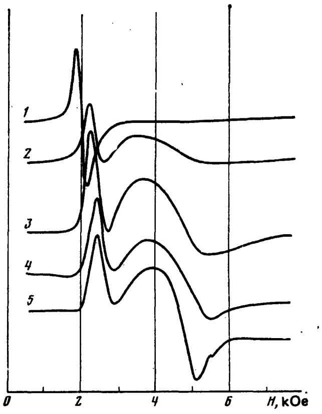

FIG. 5. Same as in Figs. 2 and 3, but with successive increases of pumping power. Specimen $2.5\times2\times0.11$ mm. P_p and t_{pump}: 1, 75 kW, 10 min; 2, 150 kW, 10 min; 3, 200 kW, 5 min; 4, 250 kW, 3 min; $\Omega=12.5$ Hz for all cases 1–4. Line 5 was recorded 2 min after the last pumping.

smoothly. With subsequent illuminations, the intensity of the new signal continued to increase, and of the original to decrease. Finally, in a sufficiently thin crystal, the original signal disappeared completely (Figs. 2 and 3). Thus the effect occurred in threshold fashion with respect to the irradiation dose.

The effect of the most powerful and prolonged pumping on AFMR in $YCrO_3$ was investigated. No effect was observed; that is, the observed effect is not due to direct excitation of Cr^{3+} ions. There are also no anomalies in optical pumping of $EuAlO_3$ with a small concentration of Cr^{3+} ions.[5] Thus the observed effect is due to interaction of Eu^{3+} and Cr^{3+} ions.

2. EXPLANATION OF THE EFFECT WITH THE COUPLED-EXCHANGE-POLARON MODEL

As was mentioned above, during relaxation it is principally the resonance field of the new signal that changes in time. But the intensity of the signal remains practically unchanged after the fast relaxation. From this fact, and also from the character of the temperature dependences (Fig. 4), it may be concluded that the observed new signal is an AFMR signal of the Cr subsystem, shifted with respect to the original signal because of an effective field that arises from interaction of the Cr^{3+} ions with excited Eu^{3+} ions that possess a magnetic moment. Here it is necessary to assume the existence of excited Eu^{3+} ions whose lifetime is very long. It is natural to seek the reason for the anomalously large lifetime in the exchange interaction of the excited Eu^{3+} ions with the magnetically ordered matrix, an interaction that did not exist when the Eu^{3+} ions were in the ground state. In the state with a magnetic moment, the Eu^{3+} polarizes the matrix, and this leads to a lowering of its energy; an "exchange polaron" appears. The existence of a power threshold and the necessity for sufficiently prolonged pumping suggest that the long-lived state is a collective state.

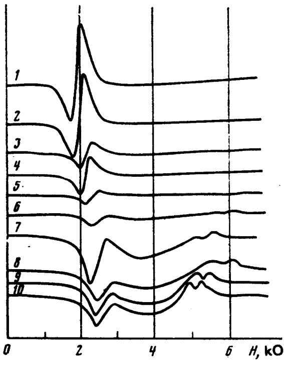

FIG. 6. Same as in Figs. 2 and 3, but with successive increases of the duration of the pumping with pulses of constant power. Specimen 2×2.5×0.11 mm, P_p = 250 kW, Ω = 12.5 Hz. 1) original AFMR signal; 2) single pumping pulse; 3) t_{pump}= 10 sec; 4) 2 min after pumping 3; 5) t_{pump}= 20 sec; 6) +40 sec (of pumping in addition to the preceding); 7) 2 min after pumping 6 (amplification through the Y channel increased); 8) + 60 sec; 9) 2 min after pumping 8; 10) 4 min after pumping 8. Sweep time of the field, 30 sec.

The large lifetime of the excited states could be understood qualitatively if we were to suppose that the energy of a state of N coupled polarons is lower than one of $N-1$ coupled polarons. In fact, in this case a transition to the ground state of a single Eu^{3+} ion is energetically disadvantageous; and of many simultaneously, improbable. Then the existence of the effect only at sufficient pumping power is explained by the necessity for simultaneous excitation of several Eu^{3+} ions located near one another. As soon as a cluster of polarons appears that can survive the time interval between pulses, the number of polarons begins to accumulate with illumination; as a result, there originates a macroregion with a shifted uniform-AFMR line.

If the thickness of the specimen is sufficiently small and the pumping power large, then this macroregion containing excited Eu^{3+} ions may occupy practically the whole volume of the crystal. This situation corresponds to the case in which the original AFMR signal completely disappears (Figs. 2 and 3).[2)] But in the case of less powerful pumping (or of a thick crystal), only part of the specimen contains excited Eu^{3+} ions. Then, of course, along with the shifted signal, the original AFMR signal should also be observed (Fig. 1 of Ref. 1; Figs. 5 and 6).

The question arises, in which one of the excited states are the Eu^{3+} ions long-lived? This may be either the state $^5D_1$, which is directly occupied in the pumping P_λ ($\lambda = 532$ nm), or one of the low-lying states $^7F_{1,2}$, to which transitions are possible according to the following schemes (Fig. 7):

$$^5D_1 \rightsquigarrow {}^5D_0 \rightarrow {}^7F_2 \rightsquigarrow {}^7F_1; \qquad {}^5D_1 \rightarrow {}^7F_1 .$$

To answer this question, the following experiment was performed. After the turning off of the pumping

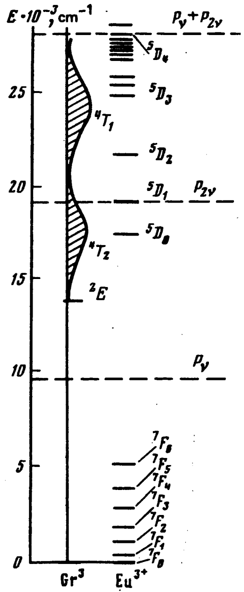

FIG. 7. Schematic representation of the optical energy levels of Cr^{3+} and Eu^{3+} ions in $EuAlO_3$. The dotted lines show the energies of quanta correpsonding to pumping at the first ($P_{2\lambda}$) and second (P_λ) harmonics of the laser and to combined application of both harmonics to the specimen.

P_λ and the fast relaxation, a second pumping $P_{2\lambda}$ ($2\lambda = 1064$ nm) was supplied to the specimen. If the long-lived state is $^5D_1$, then, as is evident from the scheme of Fig. 7, as a result of such pumping this state should be destroyed because of transitions, for example according to the following scheme:

$$^5D_1 \to {}^5D_4 \rightsquigarrow {}^5D_3 \to {}^7F_0.$$

But if the lower states ($^7F_{1,2}$) are occupied, then the pumping $P_{2\lambda}$ should not have such an effect, since at wavelength 1064 nm there are no transitions from the levels $^7F_1$ and $^7F_2$. As a result it was found that the pumping $P_{2\lambda}$, applied to the specimen after formation of the new resonance signal, produced no change under variation of the $P_{2\lambda}$ power over a broad range. If, however, both pumpings are applied simultaneously ($P_\lambda + P_{2\lambda}$), then an effect appears; but the threshold with respect to the power P_λ increases, and the intensity of the new signal is smaller than with P_λ pumping similar in power. Thus the long-lived states are $^7F_{1,2}$.[3]

We shall now demonstrate the possibility of a lowering of the energy of a cluster, consisting of several coupled polarons, with increase of the number of polarons; we shall start from a model described by the Hamiltonian

$$\mathscr{H} = N\varepsilon + \Sigma a_{\alpha\beta}(\mathbf{r}_i - \mathbf{R}_j)\mathbf{J}_i^\alpha \mathbf{S}_j^\beta + \mathscr{H}_s. \qquad (1)$$

Here N is the number of excited Eu^{3+} ions, and ε is the energy of excitation of an Eu^{3+} ion in the crystalline field without allowance for exchange. The second term describes the $3d$-$4f$ exchange; J_i^α and S_j^β are the projections of the angular-momentum operators of Eu^{3+} and Cr^{3+} respectively. $\mathscr{H}_s$ is the Hamiltonian of the chromium matrix, which is described in the usual form.[4]

The $3d$-$4f$ exchange leads not only to magnetization of the $4f$ ions by the $3d$ ions, but also to an inverse action of the $4f$ ions on the $3d$ ions. An essentially new effect that results from such inverse action is indirect exchange between the $4f$ ions via the lattice of $3d$ ions. In order to obtain the effective Hamiltonian of this exchange, we shall describe the matrix of $3d$ ions by means of a self-consistent field and shall suppose that the $4f$-$3d$ exchange is small in comparison with the $3d$-$3d$ exchange. Then, distributing the mean spin of the $3d$ ions according to an effective field

$$\mathbf{h}_j^\beta = a_{\alpha\beta}(\mathbf{r}_i - \mathbf{R}_j)\mathbf{J}_i^\alpha,$$

exerted by the $4f$ ions, we get, to the including second-order terms,

$$\mathscr{H}^{\mathrm{eff}} = N\varepsilon + \Sigma a_{\alpha\beta}(\mathbf{r}_i - \mathbf{R}_j)\mathbf{J}_i^\alpha \langle \mathbf{S}\rangle_j^\beta - {}^1/_2 \Sigma b_{\alpha\beta}(\mathbf{r}_i - \mathbf{r}_j)\mathbf{J}_i^\alpha \mathbf{J}_j^\beta. \qquad (2)$$

Here $\langle S\rangle_j^\beta$ is the mean spin of the Cr^{3+} ions, and

$$b_{\alpha\beta}(\mathbf{r}_i - \mathbf{r}_j) = \frac{v_0}{g^2\mu^2}\sum a_{\alpha\gamma}(\mathbf{r}_i - \mathbf{R}_k)\chi_{\gamma\delta}(\mathbf{R}_k - \mathbf{R}_e)a_{\delta\beta}(\mathbf{R}_e - \mathbf{r}_j), \qquad (3)$$

where v_0 is the volume per Cr^{3+} ions and $\chi_{\gamma\delta}(\mathbf{R}_k - \mathbf{R}_e)$ is the susceptibility of the $3d$ matrix.

The second term in (2) describes the effect of magnetization of the Eu^{3+} ions in the mean field of the $3d$ ions, which is nonzero in consequence of the weak ferromagnetism of the chromium subsystem. This field is small by virtue of the predominantly antiferromagnetic ordering of the chromium ions. The third term in (2) describes indirect exchange between Eu^{3+} ions via the lattice of Cr^{3+} ions. As is seen, this interaction has the same form as the $4f$-$4f$ exchange. But the exchange constant $b_{\alpha\beta}$ depends substantially on the $3d$ matrix.

The Eu^{3+} ions in EuCrO$_3$ are in a crystalline field of low symmetry (point group C_s), and therefore the spectrum of the non-Kramers ion Eu^{3+}($^7F_1$) is maximally split and consists of singlets. We shall assume that for Eu^{3+}($^7F_1$) the ground state occurs that is characteristic of all $4f$ ions in orthoferrites and orthochromates with an even number of f electrons: the lowest two singlets form a pair of levels located close together (an accidental doublet), while the third singlet is located relatively high. In this case, in the ground state we may consider a quasidoublet and describe it by means of a spin Hamiltonian with effective spin $\frac{1}{2}$. Then, as was shown by Malozemov and White,[6] only a single component of the g factor, along the axis of quantization ν, is nonzero. The axis of quantization ν lies either along the z axis or in the xy plane[4]:

$$g_\nu^{\mathrm{eff}} = (g_{xx}^2 + g_{yy}^2)^{1/2}.$$

Then the non-Kramers ions are quasi-Ising: their moments are oriented along the axis of quantization ν. With increase of temperature, under thermal population of the third and subsequent singlets, the ground state of the ions will become more isotropic, and the moments of the ions may deviate from the axis of quantization. Then it is necessary to take account of all three components of the effective g factor. We note that the relation between the components of the effective g factor reflects the relation between the components of the anisotropic exchange.[7]

And so we shall suppose that for description of the ground state of the ions Eu^{3+}($^7F_1$), only the components $a_{xx}(\mathbf{r}_i - \mathbf{R}_j)$ and $a_{yy}(\mathbf{r}_i - \mathbf{R}_j)$ are important. The longitudinal susceptibility of an antiferromagnet is usually considerably smaller than the transverse; therefore we shall take account only of the latter, which is described in the form[8]

$$\chi_\perp(q) = g^2\mu^2/v_0[A(Q) - A(q) + d]. \qquad (4)$$

Here $A(q)$ is the exchange within the $3d$ subsystem. For a simple cubic lattice ($3d$ ions in perovskite), $A(q)$ has the form[8]

$$A(q) = 2|A|N^{-1}(\cos q_x a + \cos q_y a + \cos q_z a). \qquad (5)$$

$A(Q)$ is the maximum value of $A(q)$, at the limiting value $q = Q$; d is the anisotropy constant.

We assume the condition $d/A \ll 1$. We shall also suppose that

$$a_{xx}(\mathbf{r}_i - \mathbf{R}_j) = a_{yy}(\mathbf{r}_i - \mathbf{R}_j) = a_\perp.$$

Then the Hamiltonian (3) reduces to the Hamiltonian of the XY model. We shall take into account, in it, only the self-action (exchange of a single Eu^{3+} ion with the matrix of Cr^{3+} ions, the polaron effect) and the interaction of nearest neighbors. The corresponding exchange constants are

$$b_0 = 0.46 a_\perp^2/|A|, \quad b_1 = 0.87 a_\perp^2/|A|. \qquad (6)$$

By solving the problem for a single polaron (E_1), for two coupled polarons (E_2), for a linear chain (E_3), and for four located at the vertices of a square (E_4), we get the following respective values of the energy of the ground state:

$$E_1=\varepsilon-b_0;\quad E_3=3(\varepsilon-b_0)-4b_0,$$
$$E_2=2(\varepsilon-b_0)-2{,}2b_0;\quad E_4=4(\varepsilon-b_0)-8b_0. \tag{7}$$

These values fit into the following scheme: to each polaron belongs an energy $\varepsilon-b_0$, and to each bond an energy $-2b_0$. Extrapolation of this rule to $N\gg 1$ coupled polarons gives

$$E_N=N(\varepsilon-7b_0). \tag{8}$$

Formula (8) was obtained with allowance for the fact that the Eu^{3+} ions form a cubic lattice and each Eu^{3+} ion has three bonds.

It is evident from (7) that $E_1>E_2$ when $\varepsilon<3.2b_0$; $E_2>E_3$ when $\varepsilon<2.8b_0$; $E_3>E_4$ when $\varepsilon<5b_0$. If ε corresponds to the state $^7F_1$ (~300 cm^{-1}) and if we suppose that $b_0\sim 90$ K (Fig. 4: the temperature at which the signals fuse), then the condition $E_3>E_4$ is satisfied. It is clear that the more bonds occur in a cluster at a single ion, the lower the energy of the cluster will be. In Fig. 8 are plotted, for assumed values of ε and b_0, the energies of the ground state (in units b_0) of a cluster of coupled polarons as they depend on the number of polarons. It is seen that the energy of four, eight, or twelve polarons is lower than for a cluster containing one polaron more or fewer. It is seen also that beginning with $N=24$, the energy of the clusters becomes negative; that is, the state of the crystal with coupled polarons becomes the ground state. The probability of a spontaneous transition to the new ground state is extremely small, since it requires simultaneous excitation of N Eu^{3+} ions. The lifetime of the state without polarons with respect to a transition to a state with coupled polarons is

$$\tau(\tau\varepsilon/\hbar)^{N-1}. \tag{9}$$

Here τ is the lifetime of a single Eu^{3+} ion in the state $^7F_1$, and $\Delta\varepsilon$ is the width of the $^7F_1$ level, which we have assumed to be of the order of magnitude of the level energy itself.

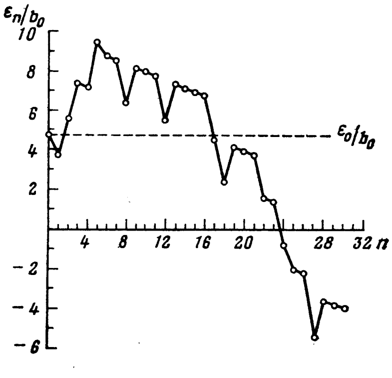

FIG. 8. Schematic representation of the energy levels of the ground state of coupled polarons. n is the number of coupled polarons; $\varepsilon=\varepsilon_0=450$ K is the energy of the state $^7F_1$ of the Eu^{3+} ion in the crystalline field; $b_0=90$ K.

Thus because of exchange interaction between Eu^{3+} ions in the state $^7F_1$ via the lattice of chromium ions, the energy of a crystal of $EuCrO_3$ is lower than for the case when the Eu^{3+} ions are nonmagnetic ($^7F_0$). But a spontaneous transition to this ground state at a low temperature is extremely improbable. At a high temperature, however, the magnetic order in the chromium subsystem is destroyed, and there is no $Eu^{3+}-Cr^{3+}$ exchange.

3. KINETICS OF FORMATION OF THE GROUND STATE

The pumping-power threshold in the occurrence of the effect is due to the fact that there must be a nonzero probability of simultaneous excitation of several Eu^{3+} ions located close together. In our model, this is sets of four Eu^{3+} ions (Fig. 8). On further pumping, there appear clusters with more and more polarons, including stable clusters, but they are still separated in space. If the pumping is turned off at this stage, the original AFMR line will not be restored in intensity because of scattering of the uniform precession by stable clusters. This situation occurs in Fig. 6 (line 4).

On further increase of the pumping time, macroregions appear with AFMR shifted with respect to field; a new resonance-absorption signal emerges, and then the whole crystal (if it is sufficiently thin) transforms to the new ground state. The formation of a new AFMR signal and the decrease of the intensity of the original one (until it disappears completely) occur within the time of duration of the pumping (Fig. 2, line 3; Fig. 5, lines 3–4).

Figure 9 (1,2) shows the time variations of the shift of the resonance field of the new AFMR with respect to the original for, respectively, a thin, completely illuminated crystal and a crystal with an interface between the new and original phases. From a comparison of the curves it is evident that relaxation proceeds faster in the thin crystal than in the crystal with an interface.

The fast relaxation at the initial instant after turning off of the laser is due, apparently, to processes of transition to the ground state of whole clusters of al-

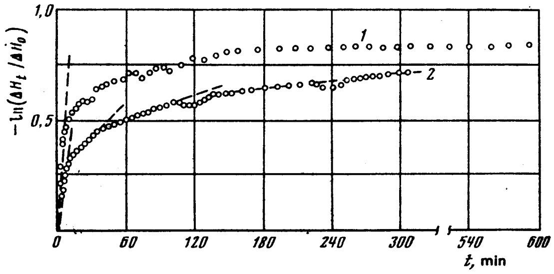

FIG. 9. Variation of $\ln(\Delta H_t/\Delta H_0)$ with time, where $H_{0,\,t}$ is the difference of the resonance field of the new AFMR signal at the instant of time t_0 or t with respect to the original value befor pumping. Signal ω_{xy}; $f=210$ GHz, $T=5$ K. Pumping parameters: $P_p=250$ kW, $\Omega=25$ Hz, $t_{pump}=240$ sec. 1) specimen thickness 0.11 mm; 2) 0.92 mm.

ready coupled polarons (at the instant of turning off of the pumping, not only the ground state of the clusters but also their excited states are populated) and to relaxation of clusters with a disadvantageous number of bonds. It is clear that during this process, spatial uniformity of the new state develops, and this leads to increase of the intensity of the new AFMR signal. But the shift of the resonance field is dependent on a change of the effective field acting on the Cr subsystem during a change either of the concentration or of the magnetic state of the Eu^{3+} ions. The ground and excited states of a cluster of N Eu^{3+} ions differ by mixture of states with different quantum numbers $M(+J, \ldots, -J)$; consequently, the magnetic state of the Eu^{3+} ions changes on transition to the ground state.

In a completely populated crystal there are, nevertheless, inhomogeneities due to defects within the crystal. Furthermore, existence of nonuniformly populated regions is possible. Relaxation of the different groups of clusters near such inhomogeneities leads to a slow shift of the AFMR field even over a period ~1.5 h. Here only the new, shifted AFMR signal will exist, while scattering by "islands" of the nonuniformly populated and the original phases will make a contribution to the width of the resonance line. With passage of time, the size of this contribution will decrease as less stable groups of clusters relax. And in fact (see Fig. 2 of Ref. 1), over a period ~1.5 h some decrease of the AFMR linewidth was observed.

In the case of a crystal with an interface between the pumped and the original phases, along with the processes described above there also occurs formation of the most advantageous interface. From Fig. 9 (2) it is seen that this process is slower, and jumps are observed after considerable intervals of time. Since for a thick crystal the intensity of illumination decreases exponentially through the thickness of the crystal, this nonuniformly illuminated part will contain, at the instant of turning off of the laser, clusters of various sizes. The clusters with an unfavorable number of bonds will relax fastest; the long-lived ones will persist: groups of four, eight, etc. (see Fig. 8). The lifetime of such clusters is large but finite. The jumps on the plot Fig. 9 (2) may be attributed to successive relaxation of groups of clusters. Such processes are accompanied by a shift of the resonance field for uniform AFMR, since during them the effective field of the Eu^{3+} ions changes with change of their concentration.

We shall now explain why a stable interface is formed, spontaneous motion of which within the unilluminated phase is practically impossible. Essentially, this occurs for the same reason that renders impossible a spontaneous transition of the crystal to a state with magnetic $Eu^{3+}({}^7F_1)$ ions. On the interface between phase, along with the relaxation processes considered, there may occur a spontaneous excitation of $Eu^{3+}({}^7F_0)$ ions to the state ${}^7F_1$. This can occur for ions that form no fewer than two bonds with the boundary of the illuminated ions (then the energy is lowered, since $\varepsilon - 5b_0 < 0$). It is clear that there occurs penetration of the boundary to a plane. If a single polaron is added to the boundary plane, the energy increases ($\varepsilon - 3b_0 > 0$). Spontaneous penetration of the boundary plane has small probability, since it requires simultaneous excitation of four adjacent Eu^{3+} ions near the boundary.

We tested whether the stability of the boundary persists when the temperature is raised. For this purpose, the specimen on which the curve of Fig. 9 (2) was taken was heated for 320 min after pumping. Both signals (corresponding to the illuminated and to the original phases) persisted during the heating; the ratio of the intensities of the signals remained essentially unchanged until their fusion at $T \sim 70$ K.[5] Apparently the process of simultaneous excitation of four ions at the phase interface has small probability at all temperatures of interest to us, when there is exchange between Eu^{3+} ions via the lattice of chromium ions.

4. NATURE OF THE NEW GROUND STATE OF $EuCrO_3$

Since, as a result of optical pumping, a new macroscopic magnetically ordered state occurs in $EuCrO_3$, the magnetic structures of the Eu and Cr subsystems must correspond to the table[9] of allowed magnetic structures for orthoferrites and orthochromites.

From the fact that the AFMR resonance field after pumping is shifted insignificantly, it follows that the Cr subsystem apparently remains in the state Γ_4. We shall analyze the possible types of ordering of the Eu^{3+} ions on the basis of the Hamiltonian (2). We shall suppose that the Eu^{3+} ions form a regular cubic lattice and that they are equivalent. But, as in the consideration of individual coupled polarons, we shall take account of the anisotropy of the $3d$-$4f$ exchange. Here, as above, we shall suppose that in the ground state only $a_{xx} = a_{yy} = a_\perp$ are important. With rise of temperature and thermal population of the third singlet, it is necessary to take account also of a_{zz}.

Since the Cr subsystem possesses a weakly ferromagnetic moment F_z, according to the second term in (2) there must arise in the Eu subsystem a "ferromagnetic" moment F_z^R in the effective field $a_{zz}F_z$. But within the temperature range in which the $Eu^{3+}({}^7F_1)$ ions are quasi-Ising, the deviation of the moments of the Eu^{3+} ions from the xy plane is insignificant, and accordingly F_z^R is small. With increase of temperature and change of the ground state of the Eu^{3+} ions, a moment $F_z^R \neq 0$ should appear.

We shall consider what kind of ordering of the Eu^{3+} ions may originate as a result of the indirect $4f$-$3d$-$4f$ exchange described by the third term in (2), with constant $b_{\alpha\beta}$ given by (3). We write the latter in the form

$$b_{\alpha\beta}(\mathbf{r}_i - \mathbf{r}_j) = \frac{v_0}{g^2\mu^2}\Big[\sum a_0^2 \chi_{\alpha\beta}(\mathbf{R}_k - \mathbf{R}_l) + \sum \delta a_{\alpha\gamma}(\mathbf{r}_i - \mathbf{R}_k)\chi_{\gamma\delta}(\mathbf{R}_k - \mathbf{R}_l)\,\delta a_{\delta\beta}(\mathbf{R}_l - \mathbf{r}_j)\Big]. \tag{10}$$

Here a_0 is the isotropic, homogeneous part of the exchange, and $\delta a_{\alpha\beta}$ is the anisotropic part of the $3d$-$4f$ exchange. For treatment of the ordering, what is of importance to us is the Fourier component

$$b_{\alpha\beta}(q) = \frac{v_0}{g^2\mu^2}\left[a_0^2\chi_{\alpha\beta}(q) + \delta a_{\alpha\gamma}(q)\chi_{\gamma\delta}(q)\,\delta a_{\delta\beta}(q)\right]. \tag{11}$$

As before, we shall take into account only $\chi_\perp(q)$ of (4) and the fact that in the ground state there is only $\delta a_\perp(q)$. We are interested in the limiting cases of ferromagnetic ($q=0$) and antiferromagnetic ($q=\pi/a$) ordering of the Eu^{3+} ions. Here we get, in the nearest-neighbor approximation,

$$b(q=0)=a_0^2/12|A|, \tag{12}$$

$$b_\perp(q=\pi/a)=(\delta a_\perp)^2/d. \tag{13}$$

It is evident that the constant of antiferromagnetic exchange is large in comparison with the ferromagnetic. In fact, in the ground state $\delta a_\perp > a_0$, while $d \ll |A|$. Thus it is to be expected that the indirect $4f$-$3d$-$4f$ exchange will lead to antiferromagnetic ordering of the Eu^{3+} ions in the xy plane. For experimental test of the considerations presented on the nature of the new ground state of $EuCrO_3$, we measured the temperature variation of the magnetization along all three axes of the crystal before and after optical pumping. The measurements were made on a vibration magnetometer with a transverse magnetic field. Oscillations of the specimen along the vertical axis, of amplitude ~1 mm, were excited at frequency 42 Hz. The moment was measured at the double frequency by means of two miniature test coils (cross section 2×0.5 mm), whose axes lay in the plane of the specimen; the specimen was placed in a horizontal plane. The same four speciments were used as in the measurement of resonance. The specimens were cemented on to the end of a cordundum holder. The holder, on a magnetic suspension, was placed in the same cryostat as in the resonance experiments.

Figure 10 shows the results of measurements of the temperature dependence of the magnetization in a magnetic field ~6 kOe. The following characteristic features are evident.

1) At temperature from 5 to 35 K, no noticeable change of the magnetization occurs after optical pumping of the crystal.[6]

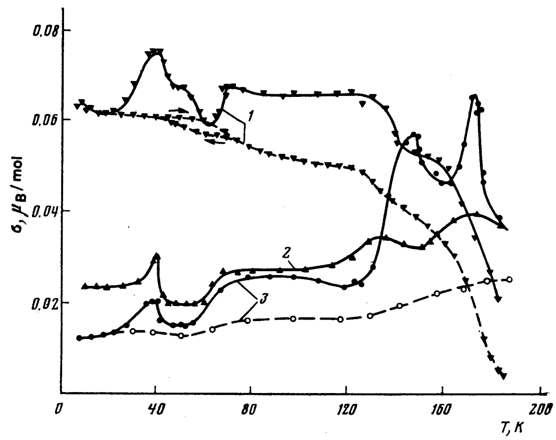

FIG. 10. Temperature dependence of magnetic moment of $EuCrO_3$, measured along axes a (Curve 2), b (Curve 3), and c (Curve 1) of the crystal. Solid lines, after pumping; dotted, before pumping. External magnetic field $H_0=5.7$ kOe. Pumping parameters P_p = 250 kW, Ω = 25 Hz, t_{pump} = 4 min.

2) In the temperature range 35–70 K, the $\sigma(T)$ relations after pumping, along all crystal axes, show anomalies that are especially pronounced at the beginning and at the end of the temperature range.

3) It is characteristic that on the $\sigma_z(T)$ relation before pumping, there is also evidence an anomaly with temperature hysteresis; but the temperature range is shifted as compared with the pumped crystal.[7]

4) On the $\sigma_y(T)$ relation at field $H_0=5.7$ kOe, an abrupt rise of magnetization is observed at $T=140$ K. A subsequent peak of the magnetization σ_y is observed at $T=180$ K, corresponding to the Néel temperature of $EuCrO_3$. On the σ_x and σ_z relations, anomalies at these temperatures are weakly manifested.

All these anomalies on the $\sigma(T)$ curves can be understood on the basis of the considerations presented above, as follows.

1) In the temperature range 5–35 K, the $Eu^{3+}(^7F_1)$ ions are quasi-Ising and are ordered antiferromagnetically because of the $4f$-$3d$-$4f$ exchange in the xy plane. The moment F_z^R of the magnetized Eu^{3+} ions is practically zero.

2) The anomalies in the temperature range 35–70 K may be due to a change of the ground state of the Eu^{3+} ion induced by thermal population of the next, third singlet in the crystalline field. Here appears a moment F_z^R of bias magnetization, and also perpendicular components of the susceptibility for the Eu^{3+} ions. We note that anomalies in the temperature dependence of the magnetization, resulting from a change of the ground state of $4f$ ions with an even number of electrons in a crystalline field, were observed earlier in $TmFeO_3$.[10]

3) The abrupt rise of the magnetization σ_y at $T=140$ K in field 5.7 kOe can be explained if we assume that the antiferromagnetic ordering of the Eu^{3+} ions because of $4f$-$3d$-$4f$ exchange occurs predominantly along the y axis of the crystal. Then at some temperature, when $H_{0y}=H_{exc}$, there should occur a metamagnetic transition, leading to an abrupt rise of the magnetization. From the AFMR data, the new signal fuses with the original when $T\approx 90$ K. But it is known that in strongly anisotropic antiferromagnets, the ordering tempera-

TABLE I. Irreducible representations of the group Pbnm.

	M^{3+}			R^{3+}		
Γ_1	A_x	G_y	C_z	—	—	C_z^R
Γ_2	F_x	C_y	G_z	F_x^R	C_y^R	—
Γ_3	C_x	F_y	A_z	C_x^R	F_y^R	—
Γ_4	G_x	A_y	F_z	—	—	F_z^R
Γ_5	—	—	—	G_x^R	A_y^R	—
Γ_6	—	—	—	—	—	A_z^R
Γ_7	—	—	—	—	—	G_z^R
Γ_8	—	—	—	A_x^R	G_y^R	—

Note. $F=S_1+S_2+S_3+S_4$, $F^R=I_5+I_6+I_7+I_8$, $G=S_1-S_2+S_3-S_4$, $G^R=I_5-I_6+I_7-I_8$, $C=S_1+S_2-S_3-S_4$, $C^R=I_5+I_6-I_7-I_8$, $A=S_1-S_2-S_3+S_4$, $A^R=I_5-I_6-I_7+I_8$.

tures are smeared out, and the ordering is extended into the temperature range $T > T_N$. For $EuCrO_3$, apparently, $90\ \text{K} < T_{\text{ord}} < 140\ \text{K}$.

4) The abrupt rise of the moment σ_y at $T = 180$ K, corresponding to T_N of the Cr subsystem, can be understood as follows. For antiferromagnetic ordering of the Eu^{3+} ions, the most effective component of the transverse susceptibility of the chromium subsystem, $\chi_\perp(q)$ of (4), is that for which the anisotropy constant d is smallest [see (13)]. It is clear that the largest anisotropy of the Cr matrix is due to the Dzyaloshinskiĭ interaction, which is absent precisely in the direction of the y axis. Hence follow two facts: first, this fact explains why ordering of the Eu^{3+} ions occurs precisely along the y axis (even if $\delta a_{xx} \approx \delta a_{yy}$); second, in the 3$d$ subsystem itself, it is this component of the susceptibility that should have, for the limiting value $q = \pi/a$, a jump near T_N, which in turn will lead to a jump of the magnetization of the Eu^{3+} ions at $T = T_N$.

5) Anomalies on the σ_z relation, without a jump, can be explained by taking into account the interaction between distantly separated thermally excited Eu^{3+} ions in the state $^7F_1$. Allowance for self-action (the polaron effect of a solitary Eu^{3+} ion), b_0 of (6), leads to the possibility of such interaction via the matrix of 3d ions. Then a change of the ground state of the Eu^{3+} ions, caused by thermal population of the third singlet, will lead also to a change of the interaction because of b_0. A temperature shift of this anomaly as compared with the pumped crystal causes no surprise, since the corresponding interaction constants are different.

Thus, by generalizing the data on the change of magnetization of $EuCrO_3$, we may conclude that in the low-temperature range (up to 35 K) the Eu^{3+} ions are ordered antiferromagnetically, predominantly along the y axis. In this temperature range, the $Eu^{3+}(^7F_1)$ ions, like the majority of non-Kramers 4f ions in orthoferrites and orthochromites, are quasi-Ising. This is suggested by the smallness of the transverse susceptibilities $\chi_{x,z}$ for antiferromagnetically ordered Eu^{3+} ions by the absence of F_z^R.

Beginning with temperatures 35 K, the ground state of the Eu^{3+} ions becomes more isotropic, and there appears a contribution to σ_z from the magnetization of the Eu^{3+} ions by the field $a_{zz}F_z$. But over the whole temperature range up to 140 K, antiferromagnetic ordering of the Eu^{3+} ions along the y axis predominates.

Turning to Table I, we note that the Cr subsystem is ordered in the structure Γ_4, while for the Eu^{3+} ions ordering of type Γ_5 or Γ_8 is possible. Admixture of a "ferromagnetic" bias magnetization of the Eu^{3+} ions along the z axis, F_z^R, corresponding to phase Γ_4, is small, but it is it that gives a slight shift of the AFMR frequency of the Cr subsystem. The analogous shift in $ErCrO_3$, where the Er^{3+} ions are magnetized only along the z axis (for $T > 10$ K), is enormous in comparison with $EuCrO_3$.[2] By processing the relations $\omega_{xy}^2(H)$ and $\omega_z^2(H)$ (Fig. 3) by the method used earlier,[2] we can obtain the value $a_{zz}F_z^R \approx -2.4$ K (at $T = 5$ K).

In conclusion, we note that the experimentally observed effect of origination of a new magnetic state in $EuCrO_3$, as a result of high-power optical pumping, is explained by taking into account the effective exchange interaction between the Eu^{3+} ions via the lattice of Cr^{3+} ions. The results of this paper show that this interaction not only exists, but is not weak when the 3d matrix is antiferromagnetic.

The authors are grateful to G.A. Smolenskiĭ for his attention to the research, to A.S. Borovik-Romanov for useful discussions, and to B.D. Laikhtman for fruitful discussions during the process of research.

[1] This is due to the fact that, as will be seen from the later discussion, in our experiments the greater part of the absorbed light power is reradiated. At high temperatures the fraction of the energy going into heating of the specimen increases.

[2] For maximum pumping (~100 sec with pumping parameters $P_p = 250$ kW, $\tau_p = 15$ ns, $\Omega = 25$ Hz), the total number of pumping quanta is $N \sim 10^{20}$. The total number of Eu^{3+} ions in the specimen $\sim 10^{19}$. The coefficient of absorption of light at $\lambda = 532$ nm is 70 cm^{-1}. Thus the power is sufficient for excitation of all the Eu^{3+} ions if the thickness of the specimen is sufficiently small ($\lesssim 0.15$ mm).

[3] It will be shown below that the conditions for an anomalously long lifetime of the Eu^{3+} ion are satisfied only for the state $^7F_1$.

[4] It is this case that will be of interest to us, since, as we shall see later, it is the one that occurs in $EuCrO_3$.

[5] The difference between the temperatures of fusion of the signals for the thick crystal (70 K) and for the thin (90 K) is due mainly to a difference in the width of the resonance line. For the thick crystal, the AFMR linewidth is considerably larger, and the signals become unresovable at 70 K.

[6] Figure 10 shows the $\sigma(T)$ relation taken 15 min after the turning off of the laser. In the first few minutes after the turning off, just as for the shift of the resonance field, a time variation of the $\sigma(T)$ relation is observed—fast relaxation.

[7] The measurements of $\sigma_z(T)$ without pumping were made, also on a standard vibration magnetometer, by S. A. Kizhaev, to whom the authors express their gratitude.

---

[1] E. I. Golovenchits, B. D. Laĭkhtman, and V. A. Sanina, Pis'ma Zh. Eksp. Teor. Fiz. **31**, 243 (1980) [JETP Lett. **31**, 223 (1980)].

[2] E. I. Golovenchits and V. A. Sanina, Zh. Eksp. Teor. Fiz. **69**, 1301 (1975) [Sov. Phys. JETP **42**, 665 (1975)].

[3] K. Tsushima, I. Takemura, and S. Osaka, Solid State Commun. **7**, 71 (1969).

[4] E. I. Golovenchits and V. A. Sanina, Fiz. Tverd. Tela (Leningrad) **17**, 2837 (1975) [Sov. Phys. Solid State **17**, 1900 (1965)].

[5] J. P. van der Ziel and L. G. Van Uitert, Phys. Rev. **B8**, 1889 (1973).

[6] A. P. Malozemoff and R. L. White, Solid State Commun. **8**, 665 (1970).

[7] T. Moriya, in: Magnetism, Vol. I. ed. G. T. Rado and H. Suhl, Academic Press, 1963, Chap. 3, p. 85.

[8] R. M. White, Quantum Theory of Magnetism, McGraw-Hill, 1970, Chap. 4 (Russ. transl., Mir, 1972).

[9] E. F. Bertaut, in: Magnetism, Vol. III, ed. G. T. Rado and H. Suhl, Academic Press, 1963, Chap. 4, p. 149.

[10] J. A. Cape and A. P. Malozemoff, Solid State Commun. **8**, 2067 (1970).

Translated W. F. Brown, Jr.