Optical-magnetic resonance and relaxation of Tm^{2+} in CaF_2

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We investigated the optical-magnetic resonance (OMR) of Tm^{2+} in CaF_2 at $T = 1.7°K$. To study the relaxation kinetics in the system of magnetic sublevels of the ground state, the measurements were performed on crystals with various Tm^{2+} concentrations ($C = 0.019$, 0.031, 0.096, and 0.12 mol.%). An analysis of the OMR spectra (lines in the field H_0) has yielded the probability ratio of the four types of relaxation transitions that take place in a four-level system ($S = 1/2$, $I = 1/2$) for each of the investigated concentrations. It is found that as the concentration increases from 0.019 to 0.12 mol.% a sharp increase takes place in the probability of the relaxation transitions between the sublevels corresponding to different orientations of the nuclear spin moments at one and the same orientation of the electron spin moment; this is equivalent to a unification of the Zeeman and electron dipole-dipole reservoirs. An additional OMR spectrum was observed in a magnetic field $H = H_0/2$. An investigation of the dependence of the intensity of this spectrum on the change of the microwave pump level has made it possible to determine the probabilities of the transitions corresponding to the given lines. It is shown that these lines are satellites at double the frequency and result from the nonsecular part of the dipole-dipole interaction.

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Paramagnetic Tm^{2+} centers in CaF_2 were previously investigated by the EPR method and by the magneto-optical method.[1-3] It was observed that in the EPR spectrum obtained by optical detection (the optical-magnetic resonance (OMR) spectrum) contains, besides the principal doublet connected with the hyperfine splitting by the Tm^{169} nucleus, also lines in a weaker magnetic field, interpreted as lines of complexes (pairs, triads) of Tm^{2+}. Jeffries[2] paid principal attention to questions of nuclear polarization in saturation of EPR transitions, and assumed that the system of relaxation transitions in the Tm^{2+} level scheme is preserved at the paramagnetic-center concentrations used in[2]. We have investigated the OMR of TM^{2+} in CaF_2 at a different TM^{2+} concentration in order to assess the kinetics of the relaxation in this system.

1. THE METHOD

We investigated the OMR by a procedure based on measuring the rotation of the plane of polarization of light (the Faraday effect) following saturation of the EPR transitions.[4] In this case the rotation of the polarization plane by the sample is due to additive contributions from different paramagnetic centers contained in the sample, whereas the EPR conditions are selective. Even if the sample contains paramagnetic centers of only one sort, the inhomogeneous broadening of the EPR line will cause only a fraction of the paramagnetic centers to interact resonantly with the microwave power at each given value of H_0 or $h\nu_0$.

At low temperatures ($T \approx 1.7°K$) the paramagnetic rotation of the polarization plane predominates, and the rotation angle is proportional to the difference between the populations of the magnetic sublevels of the ground states of the paramagnetic ions present in the sample. Saturation of the EPR transition equalizes the populations of the sublevels of the resonant paramagnetic centers, and the rotation of the polarization plane decreases accordingly. If the sample contains centers of only one type and they differ only because of the inhomogeneous broadening (say owing to the hyperfine interaction), then the change of the Faraday rotation of the polarization plane when the EPR of an individual group of centers (of each hyperfine component of the spectrum) is saturated will be determined by the number of centers in the given group (by the corresponding nuclear population) and by the cross relaxation between the given centers and other centers present in the sample, while the power level at which saturation is reached will characterize the probability of the EPR transition in the given group of centers.

The polarization-plane rotation angle depends also on the wavelength of the light. But if the sample contains paramagnetic centers of only one type and the diamagnetic rotation of the polarization plane is negligibly small, the relative change of the rotation upon saturation of a single EPR line will not depend on the light wavelength at which the measurements are made. In the crystals investigated by us (according to the given criterion) there were practically no paramagnetic centers other than Tm^{2+}—the relative change of the rotation produced when various EPR spectral lines were saturated did not change with the wavelength of the light, except for the sections where the paramagnetic rotation reversed sign and the diamagnetic contribution became noticeable. It can therefore be assumed that the changes of the polarization plane following EPR saturation carry information on the populations of the sublevels of the ground state and are determined by the relaxation processes and by the EPR pumping.

2. EXPERIMENT

We investigated CaF_2:Tm samples with Tm^{3+} concentration in the initial mix $C \approx 0.019$, 0.031, 0.096, and 0.12 mol.%. The Tm^{3+} ion was charge-exchanged into Tm^{2+} by additive coloring and (or) x-rays. The

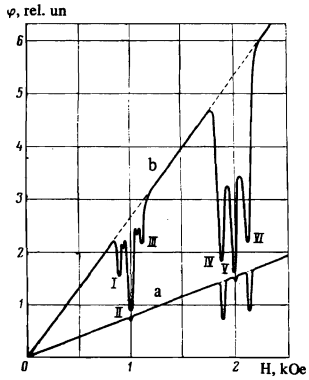

FIG. 1. Plot of Faraday rotation signal $\varphi(H)$ in samples with different Tm^{2+} concentrations in CaF_2 at a maximum microwave pump power: a) $C \approx 0.019$ mol. %, b) $C \approx 0.12$ mol. %, $\lambda_{det} = 5000$ Å, T = 1.7°K.

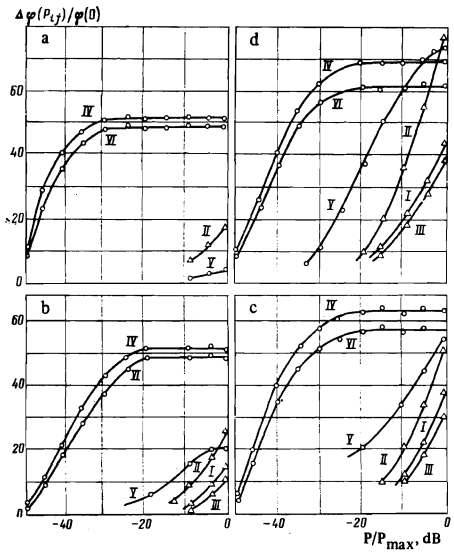

FIG. 2. Relative values of $\Delta\varphi(P_{ij})/\varphi(0)$ of the EPR dips I–VI (see Fig. 1) vs the microwave power level at the $CaF_2:Tm^{2+}$ samples: a) $C \approx 0.019$ mol. %, b) $C \approx 0.031$ mol. %, c) $C \approx 0.096$ mol. %; d) $C \approx 0.12$ mol. %.

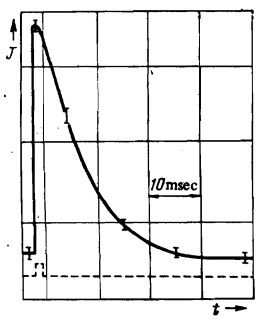

FIG. 3

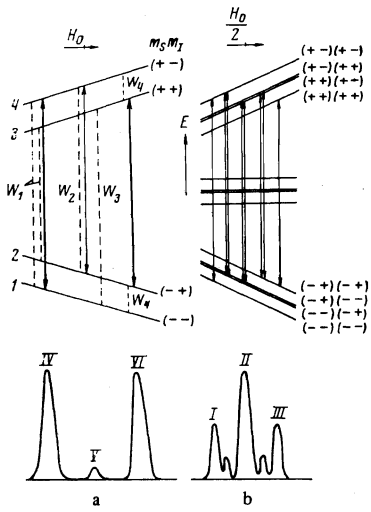

FIG. 4

FIG. 3. Oscillogram of the intensity $J(\varphi)$ of light passing through the sample in an optical system with crossed polarizers, at H corresponding to one of the EPR lines. The dashed line shows the time dependence of the microwave power.

FIG. 4. Tm^{2+} ground-state energy levels corresponding to the investigated transitions: a) energy levels, EPR transition (solid lines), and possible relaxation transition (dashed lines) of a single paramagnetic Tm^{2+} center near the field H_0; b) energy levels and possible EPR transitions of two Tm^{2+} ions coupled by dipole-dipole interaction. The regular wave functions for the degenerate states are superpositions of the functions shown in the figure.

OMR spectra obtained in both cases were identical, with the exception of effects that depended on the Tm^{2+} concentration. Additive coloring yielded a higher Tm^{2+} concentration, as seen from the spectra. The EPR spectrum obtained with a 3-cm EPR spectrometer is a doublet described by the spin-Hamiltonian

$$\mathcal{H} = g\beta HS + AS I, \qquad (1)$$

where the parameters $g = 3.453$, $|A| = 1101$ MHz, $S = 1/2$, and $I = 1/2$ agree fully with the data of[1]. The sign of the constant A is known from Ritter's work[5]: $A = -1101$ MHz. At the center of the doublet there was observed a (much weaker) line corresponding to the forbidden transition ($\Delta m_S = \pm 1$, $\Delta m_I = \mp 1$).

The OMR plots at saturating microwave power are shown in Fig. 1 for two different concentrations of the paramagnetic centers. It is seen that besides the lines observed in the usual EPR spectrum there is a group of lines at approximately half the field strength. The additional spectrum is practically isotropic. Five lines are distinctly seen, three of them stronger. For these three lines, and also for the lines of the main spectrum, we investigated the dependence of the Faraday-rotation angle, following application of microwave power, on the value of this power (see Fig. 2). In addition, relaxation of the magnetic-sublevel population distribution was revealed by restoration of the rotation of the polarization plane after the termination of the microwave time. The restoration time, measured for all lines of the observed spectrum, was the same within the limits of errors and was independent of the concentration; a typical oscillogram is shown in Fig. 3.

3. DISCUSSION

The level scheme of the ground state of Tm^{2+} ($S = 1/2$, $I = 1/2$) in a strong magnetic field and the possible relaxation transitions are shown in Fig. 4a. We assume from the very outset that the relaxation probabilities are $W_{1-4} \approx W_{2-3} = W_1$ and $W_{1-2} \approx W_{3-4} = W_2$. The off-diagonal terms of the hyperfine interaction parameter mix the states 2 and 4, as a result of which the relaxation probability is $W_{2-4} = W_2 > W_{1-3} = W_3$. For the same reason, EPR transitions can appear between levels 2 and 4.

The rotation angle φ of the plane of polarization of the light (paramagnetic rotation) is proportional to $N_1 + N_2 - N_3 - N_4$, where N_i is the population of the corresponding sublevel. If any of the possible EPR transitions is fully saturated, the populations of the levels between which the transition takes place become equalized, and the populations of the remaining levels are determined by the probability ratio of the relaxation transitions. The polarization plane rotation angle remains constant in this case. It is convenient to consider the quantity $\Delta\varphi(P_{ij})_{max}/\varphi(0)$, where $\Delta\varphi(P_{ij})_{max}$ is the change of the rotation angle under saturating microwave pumping of the transition between the levels i and j, and $\varphi(0)$ is the rotation angle in the absence of microwave pumping. In this case

$$\frac{\Delta\varphi(P_{ij})}{\varphi(0)} = \left| 1 - \frac{N_1(P_{ij}) + N_2(P_{ij}) - N_3(P_{ij}) - N_4(P_{ij})}{N_1(0) + N_2(0) - N_3(0) - N_4(0)} \right|. \qquad (2)$$

The populations corresponding to stationary saturating pumping can be expressed in terms of the ratio of the relaxation probabilities when solving the system of equations for the populations. For extremely low con-

centrations, when the interaction between the Tm^{2+} ions is negligible. The assumption $W_1 \gg W_2 \gg W_3, W_4$ is valid and leads to the following calculated values:

$$\frac{\Delta\varphi(P_{1\leftrightarrow4})_{max}}{\varphi(0)}=50.3\%,\quad \frac{\Delta\varphi(P_{2\leftrightarrow3})_{max}}{\varphi(0)}=50.9\%,\quad \frac{\Delta\varphi(P_{2\leftrightarrow4})_{max}}{\varphi(0)}=-0.87\%.$$

Comparing these figures with the results shown in Fig. 2 at the microwave powers for which curves IV, V, and VI have already reached saturation, we see that the obtained relations are not satisfied, although the values of $\Delta\varphi(P_{ij})_{max}/\varphi(0)$ at minimum concentration are closest to the calculated ones. Obviously, the interaction between the Tm^{2+} ions leads to an effective change in the relaxation probabilities.

Let us examine this dependence qualitatively. We denote the probability ratio of the relaxation transitions shown in Fig. 4a by

$$W_2/W_1=K_2,\quad W_3/W_1=K_3,\quad W_4/W_1=K_4.$$

The role of the dipole-dipole interaction, which leads to cross-saturation of the hyperfine components of the EPR spectrum, manifests itself in such a scheme effectively as an increase of the coefficient K_4 with increasing Tm^{2+} concentration; this is equivalent to the formation of a common dipole and hyperfine reservoir, in analogy with the results obtained in[6]. This situation should obtain at concentrations such that the probability W_1 (which determines mainly the rate of saturation relaxation) is determined by one-ion processes and is independent of the concentration, in accord with our experimental results. For W_2 there is also a one-ion relaxation mechanism, whereas for W_3 there is none, so that the coefficient K_2 should depend less on the concentration than K_3, and both should have a weaker dependence on the concentration than K_4. Solving the equation for the populations we can find the K_2, K_3, and K_4 corresponding to the experimentally observed values of $\Delta\varphi(P_{ij})_{max}/\varphi(0)$.

We write down the equations for the stationary populations ($dN_i/dt = 0$) at microwave pumps P_{1-4}, P_{2-3}, and P_{2-4}. Equation (2), together with the requirement that the number of paramagnetic centers remain unchanged and that $N_i(P = 0)$ have a Boltzmann distribution, enable us to express the populations of the levels unaffected by the pump in terms of the population of the pumped levels $N_i(P_{ij}^{max}) = N_j(P_{ij}^{max})$ and the in terms of $\Delta\varphi(P_{ij})_{max}/\varphi(0)$. Then, discarding the equations for the populations of the pumped levels, we obtain six equations for the quantities K_2, K_3, K_4,

$$N_1(P_{1\leftrightarrow4}^{max})=N_4(P_{1\leftrightarrow4}^{max}),\ N_2(P_{2\leftrightarrow3}^{max})=N_3(P_{2\leftrightarrow3}^{max})\text{ and }N_2(P_{2\leftrightarrow4})=N_4(P_{2\leftrightarrow4}).$$

These equations contain the following parameters: the temperature, spectrometer frequency, hyperfine-splitting constants, and three experimental values of $\Delta\varphi(P_{ij})_{max}/\varphi(0)$ for three types of microwave pumping. There are no free parameters.

Computer solution of the equations has shown that K_4 is determined quite accurately, but K_2 and K_3 are very sensitive to the accuracy with which $\Delta\varphi(P_{ij})/\varphi(0)$ is determined (i.e., this ratio depends strongly on K_4 and little on K_2 and K_3). Therefore at the experimental accuracy with which we determined the ratio $\Delta\varphi(P_{ij})_{max}/\varphi(0)$, namely $\approx \pm 1.5\%$, we obtained for each concentration a definite value of K_4 and a branch of interrelated values of K_2 and K_3, within which each of these quantities varies in a range of $\approx 50\%$. The obtained values are listed in Table I.

TABLE I. Experimental values of $\Delta\varphi(P_{ij})_{max}/\varphi(0)$ and calculated ratios of the probabilities of the relaxation transitions

C, mol. % (initial mix)	$\frac{\Delta\varphi(P_{ij})_{max}}{\varphi(0)}$, %			K_4	K_2	K_3
	P_{14}	P_{23}	P_{24}			
0.019	51±1.5	47±1.5	7±1.5	0.04	0.16 *	0.05
0.031	52±1.5	49±1.5	20±1.5	0.2	0.7 *	0.06
0.096	66.5±1.5	54±1.5	66±1.5	1.0±0.05	0.1÷0.25	0.25÷0.15
0.12	67.5±1.5	58±1.5	72±1.5	1.0±0.05	0.1÷0.25	0.25÷0.15

*These quantities are determined with the least accuracy.

We consider now the absorption lines in the half-value field. The lines I, II and III in the half-value field are characterized by the following: 1) $\Delta\varphi(P)/\varphi(0)$ is not in the least saturated at the employed powers; 2) $\Delta\varphi(P)/\varphi(0)$ increases with increasing Tm^{2+} concentration;[3] the relaxation of $\Delta\varphi(P)$ when the microwave pulse terminates obeys practically the same law and occurs in the same time as the main EPR transitions; 4) the dependence of $\Delta\varphi(P)/\varphi(0)$ on the light wavelength at which the measurement is made is the same as for the main lines of the spectrum; 5) the splitting (in terms of the magnetic field) between lines I and III is equal to the splitting between the hyperfine components of the main doublet (IV, VI); finally 6) the values of $\Delta\varphi(P)_{max}/\varphi(0)$ are of the same order as for the main lines of the spectrum. We can therefore conclude that the EPR transitions pertaining to these lines lead to equalization of the populations in the system of the sublevels of the main paramagnetic impurity (Tm^{2+}), and the probability of a transition in the system of the Tm^{2+} sublevels as a result of absorption in these lines is much lower than direct absorption in the main EPR spectrum of Tm^{2+}.

Similar transitions can result from interaction between the Tm^{2+} ions. In particular, the nonsecular part of the dipole-dipole interaction operator should lead to a simultaneous transitions in two ions near double the Larmor frequency,[7] i.e., in the half-value field. Figure 4b shows the level scheme and the possible transitions in a system of two Tm^{2+} centers coupled by dipole-dipole interaction, with account taken of the off-diagonal part of the hyperfine interaction. If the sublevel splitting connected with the dipole-dipole interaction is much less than the EPR line width due to the hyperfine interaction of the Tm^{2+} with the surrounding F^- ions, then the observed EPR spectrum should correspond to that shown in Fig. 4b, in accord with the experimentally observed OMR spectrum.

Let us estimate the expected transition probabilities for these lines. We start with the results of Konovalov and Ryabchenko,[8] who calculated the intensities and second moments of the satellites connected with the off-diagonal part of the dipole-dipole interaction. According to these results, in EPR measurements at fixed frequency (with a scanned magnetic field), the ratio of the integral transition probability of the satellite in a half-value field (at double the frequency) to the transition probability in the main line of the spectrum should equal, for a polycrystalline sample,

$$M = {}^3/_5\beta^2g^2H^{-2}(S+1)\sum_{j'}{}' r_{ij'}^{-6}. \qquad (3)$$

Here H is the field in which satellites and "double the

TABLE II. Ratio of the probabilities of the EPR transitions of lines I, II, III, and V to the transition probability of the main line IV

C, mol.%	Probability ratio, dB							
	Line I		II		III		IV	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
0.019	−39.4	–	−39.4	48 *	−39.4	–	−18.5	20±2
0.031	−37.45	43 *	−37.45	43 *	−37.45	43 *	−18.5	20±2
0.096	−32.2	39 *–42 **	−32.2	39 *–42 **	−32.2	39 *–42 **	−18.5	20±2
0.12	−31.25	34 *–39 ***	−31.25	34 *–39 ***	−31.25	34 *–39 ***	−18.5	20±2

*Obtained at $\Delta\varphi(P_{ij})/\Delta\varphi(P_{ij})_{max} = 0.22$.
**Obtained at $\Delta\varphi(P_{ij})/\Delta\varphi(P_{ij})_{max} = 0.5$.
***Obtained at $\Delta\varphi(P_{ij})/\Delta\varphi(P_{ij})_{max} = 0.62$.

requency" i.e., $H_0/2$, are observed. The prime on the summation sign means summation only over the sites occupied by paramagnetic impurities. In the case of an equally-probable impurity distribution we have

$$\sum_{j'}{}' r_{ij'}^{-6} = C \sum_{j}{}' r_{ij}^{-6}, \qquad (4)$$

where C is the molar concentration of the impurity, and the summation in the right-hand side is over all the lattice sites.

An estimate of $\sum' r_{ij}^{-6}$ in the CaF_2 crystal yields a value $\sim 25 \times 10^{44}$ cm^{-6}, leading to the value $M = C \cdot 1.25$. If we now take into account the spectrum structure in the half-value field (Fig. 4b), we find that the ratio of the transition probability for lines I, II, or III to the probability of the transition of one of the lines of the allowed hyperfine doublet (IV or VI) will equal M/2. Then complete saturation of the line I (III) (EPR transitions only for ions with one of the projections of I_z) should lead to the same change of the Faraday-rotation angle as complete saturation of the line IV (VI), whereas complete saturation of line II (EPR transitions for ions with both projections of I_z) should lead to 100% "burnout" of the paramagnetic Faraday rotation. The transition probabilities for the weak lines located between lines I and II and between II and III should be less than the transition probabilities for lines I, II, and III by a factor $(2A/g\beta H_0)^2$, whereas the ratio of the transition probability for line V to the probabilities for lines IV and VI should amount to $A/g\beta H_0$, and this yields respectively ~ 0.04 and ~ 0.01. Naturally, in ordinary EPR no lines can be observed in the half-value field because of the very low transition probability, but in the OMR spectrum they will be observed at sufficiently high microwave power.

Since all the ions in the crystal are coupled by dipole-dipole interaction, practically all the Tm^{2+} centers can be saturated. However, since the Tm^{2+} distribution over the sample cannot be strictly homogeneous, the populations of the sublevels of the Tm^{2+} centers, located in places with different local concentrations, will be saturated at different power levels, and this will lead to delay the onset of saturation on the $\Delta\varphi(P)/\varphi(0)$ curve. In all probability, an investigation of the $\Delta\varphi(P)/\varphi(0)$ curves of paired transitions can be used to analyze the distribution of the centers in the sample. At equally probable Tm^{2+} distribution, the probability of two-particle transitions should be proportional to the concentration.

The ratio of the probability of the paired transition to the probability of the ordinary EPR transition can be determined by measuring the ratio of the microwave powers at which the same ratio $\Delta\varphi(P)/\Delta\varphi(P)_{max}$ is reached for both transitions. To obtain this probability ratio from the saturation curves (Fig. 2), we plotted $\Delta\varphi(P)/\Delta\varphi(P)_{max}$ for lines I–VI. For lines I and III the ratio $\Delta\varphi(P)_{max}/\varphi(0)$ was assumed equal to the analogous value for lines IV and VI, and for line II we assumed $\Delta\varphi(P)_{max}/\varphi(0) = 100\%$. The resultant probability ratios, together with the calculated quantities (it was assumed in the calculation that additive coloring leads to 100% charge exchange of Tm^{3+}, and therefore the Tm^{2+} concentration is the same as the concentration in the initial mix) are listed in Table II.

The scatter of the experimental values corresponds to a higher relative pair-spectrum probability in the initial sections of the saturation curves than in the central sections of the same curves, as is to be expected in the case of an inhomogeneous impurity distribution. The reason why the experimentally obtained probability ratio is systematically lower by 6–8 dB than the calculated one is obviously that the real Tm^{2+} concentration obtained after additive coloring is lower by five to eight times than the Tm^{2+} concentration obtained after additive coloring is lower by five to eight times than the Tm^{2+} concentration in the initial mix used to grow the crystal.

Thus, as a result of our investigations we were able to obtain the concentration dependence of the probability ratios of the relaxation transitions in the Tm^{2+} level system and to demonstrate the dipole-dipole character of the satellites lines in the half-value field. It should be noted that it is hardly possible to obtain this information without using the OMR technique.

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[1] R. G. Bessent and W. Hayes, Proc. R. Soc. **A285**, 430 (1965).
[2] C. D. Jeffries, Phys. Rev. Lett. **19**, 1221 (1967); transl. in: Paramagnitnyĭ rezonans (Paramagnetic Resonance), Nauka, 1971, p. 31.
[3] C. H. Anderson, H. A. Weakleim, and E. S. Sabisky, Phys. Rev. **143**, 223 (1966).
[4] A. V. Komarov and C. M. Ryabchenko, Prib. Tekh. Eksp. No. 4, 201 (1971).
[5] G. J. Ritter, Phys. Rev. **128**, 2238 (1962).
[6] V. A. Atsarkin, A. E. Mefed, and M. I. Rodak, Zh. Eksp. Teor. Fiz. **55**, 1671 (1968) [Sov. Phys.-JETP **28**, 877 (1969)]; B. A. Atsarkin, M. I. Zhabotinskiĭ, A. E. Mefed, S. K. Morshnev, and M. I. Rodak, in: Paramagnitnyi rezonans (Paramagnetic Resonance), Nauka, 1971, p. 38.
[7] J. H. Van Vleck, Phys. Rev. **73**, 1249 (1948).
[8] V. I. Konovalov and S. M. Ryabchenko, Fiz. Tverd. Tela **8**, 3541 (1966) [Sov. Phys. Solid State **8**, 2833 (1967)].

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101