SOVIET PHYSICS JETP VOLUME 15, NUMBER 1 JULY, 1962

SPIN-LATTICE RELAXATION AND CROSS-RELAXATION INTERACTIONS IN CHROMIUM CORUNDUM

A. A. MANENKOV and A. M. PROKHOROV

P. N. Lebedev Physics Institute, Academy of Sciences, U.S.S.R.

Submitted to JETP editor July 31, 1961

J. Exptl. Theoret. Phys. (U.S.S.R.) **42**, 75-83 (January, 1962)

Relaxation phenomena in chromium corundum ($Al_2O_3 \cdot Cr_2O_3$) single crystals were studied at liquid helium temperatures and a frequency of 9400 Mc by the pulse technique. The spin-lattice relaxation times were determined for samples with various Cr^{3+} concentrations. Spin-spin cross-relaxation interactions were discovered in the spectrum and were investigated for various splitting ratios between the Cr^{3+} ion energy levels. The times and amplitudes of the exponentials characterizing the cross-relaxation interactions were determined for a sample having a Cr^{3+} concentration of 0.15%. An interpretation of the results is presented.

1. INTRODUCTION

THE establishment of thermal equilibrium between the spin system of paramagnetic ions and the lattice, as well as within the spin system, plays an important role in crystals that are used to achieve negative temperatures in the energy level system. In view of this there has been a marked growth of interest in recent years in the investigation of relaxation phenomena in paramagnetic crystals, particularly at low temperatures. Several investigations of relaxation in crystals have found practical application in paramagnetic quantum amplifiers. This research, stimulated by the practical considerations of quantum electronics, has, in its turn, led to the development of the theory of paramagnetic relaxation. In particular, Bloembergen and others[1] have developed a theory of spin-spin cross-relaxation, which, as confirmed by several experiments, plays an extremely important role in the processes that establish thermal equilibrium within a spin system with many energy levels.

Kochelaev[2] and Anderson[3] have undertaken also to develop theories of spin-lattice relaxation. Although some of the peculiarities of paramagnetic relaxation at low temperatures have been qualitatively explained on the basis of cross-relaxation, a more detailed investigation of both cross-relaxation interactions and spin-lattice relaxation in paramagnetic crystals is needed.

The object of the present work was the detailed study of the relaxation phenomena in the spectrum of Cr^{3+} in monocrystals of corundum (Al_2O_3) at liquid helium temperatures. The relaxation of Cr^{3+} in Al_2O_3 has been the subject of many previous studies.[4-10] In our first paper,[4] devoted to the investigation of spin-lattice relaxation of Cr^{3+} in Al_2O_3, the continuous saturation method was used. This method is an indirect one for the determination of the spin-lattice relaxation time T_1, for to calculate T_1 from the saturation parameters determined directly from the experiments, it is necessary to know the spin-spin relaxation time T_2 and the transition probability for the observed paramagnetic resonance line, and also the intensity of the high-frequency field causing the saturation. Besides, it is difficult to separate the effects of spin-lattice and spin-spin cross-relaxation in this method.

In the present more detailed investigation of spin-lattice and cross-relaxation we have therefore used the pulse method of saturation of the paramagnetic resonance line. The pulse method is a direct one for measuring the relaxation times and permits the separation of spin-lattice and cross-relaxation effects, through the use of different pulse lengths. Because of this, it is possible to determine the spin-lattice relaxation and cross-relaxation times T_1 and T_{12} and to separate the dependence of T_1 and T_{12} on the paramagnetic ion concentration and temperature.

2. METHOD AND EXPERIMENTAL CONDITIONS

The experiments to study the relaxation of Cr^{3+} in Al_2O_3 were carried out with a superheterodyne spectrometer at 9400 Mc and liquid helium temperatures. The pulse method described earlier[11] was used. Saturation of the paramagnetic resonance line was produced by pulses varying in length from 0.8 millisec to 1 sec. Monocrystals of corundum with the following concentrations of Cr^{3+} ion relative to the diamagnetic Al^{3+} ions were studied: 0.05, 0.1, 0.15, 0.4, and 0.65%. The sample with 0.15% concentration was studied in much more detail because a strong manifestation of the cross-relaxation effect was observed in the region of concentrations from 0.1 to 0.15%.

3. THEORETICAL TREATMENT OF CROSS-RELAXATION BETWEEN Cr^{3+} LEVELS

In the lowest ground state of a Cr^{3+} ion situated in the crystalline field of the Al_2O_3 lattice and an external magnetic field there are four spin energy levels, corresponding to the electronic spin $S = 3/2$. The rigorous analysis of the relaxation processes in such a system, taking into account the relaxation transitions evoked by the spin-lattice and spin-spin interactions, is quite complicated. However, certain rules concerning cross-relaxation in a system of four levels can be deduced by means of a simplified scheme. In this scheme we regard the system as made up of two pairs of levels E_1, E_2 and E_3, E_4, between which a spin-spin cross-relaxation is established, but the spin-lattice transitions proceed only within each pair of levels; for simplicity we assume that these transitions occur at the same rate (identical spin-lattice relaxation times for both pairs of levels).

Thus, in this simplified scheme we are neglecting the spin-lattice transitions between the levels 1 and 3, 1 and 4, 2 and 3, and 2 and 4. In the real system of levels of Cr^{3+} such neglect is valid when the probabilities of the indicated spin-lattice transitions is much less than the probabilities of the cross-relaxation transitions between the levels 1 and 2 or 3 and 4. If the splittings between the levels have a whole-number ratio $E_4 - E_3 = m(E_2 - E_1)$, $m = 1, 2, 3, \ldots$, then the cross-relaxation between the level pairs E_1, E_2 and E_3, E_4 can occur on account of the simultaneous transitions of two (when $m = 1$) or more (when $m = 2, 3$) ions between which a spin-spin interaction exists. The total energy of the spin system is not changed by such cross-relaxation transitions.

Figure 1 shows a level scheme in which the splitting ratio is $m = 2$. In this system cross-relaxation can take place in the following way: a change in the orientation of the spin of one ion (transition from level 3 to level 4) is accompanied by a simultaneous change of orientation of the spins of two neighboring ions (transitions from level 2 to level 1). For the population differences we have the following kinetic equations:

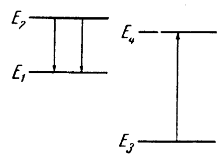

FIG. 1. Cross-relaxation transitions in a four-level system.

$$\frac{d(n_1 - n_2)}{dt} = -\frac{1}{T_1}(n_1 - n_2 - n_1^0 + n_2^0) + w_{cr}(n_2^m n_3 - n_1^m n_4) - 2W(n_1 - n_2),$$

$$\frac{d(n_3 - n_4)}{dt} = -\frac{1}{T_1}(n_3 - n_4 - n_3^0 + n_4^0) - \frac{w_{cr}}{m}(n_2^m n_3 - n_1^m n_4), \tag{1}$$

where n_i $(i = 1, 2, 3, 4)$ is the population of the energy level at thermal equilibrium, T_1 is the spin lattice relaxation time, w_{cr} is the probability of cross-relaxation, and W is the probability of the 1 → 2 transition induced by the external high-frequency field.

When the separation between the levels is less than kT, Eq. (1) can be rewritten in the form

$$\frac{d\Delta n_{12}}{dt} = -\frac{1}{T_1}(\Delta n_{12} - \Delta n_{12}^0) + w'_{cr}(\Delta n_{34} - \beta\Delta n_{12}) - 2W\Delta n_{12},$$

$$\frac{d\Delta n_{34}}{dt} = -\frac{1}{T_1}(\Delta n_{34} - \Delta n_{34}^0) - \frac{w'_{cr}}{m}(\Delta n_{34} - \beta\Delta n_{12}), \tag{2}$$

where

$$\Delta n_{ij} = n_i - n_j, \quad w'_{cr} = w_{cr} n_2^m \approx \text{const}, \quad \beta = \Delta n_{34}^0 / \Delta n_{12}^0.$$

When the probability of transitions induced by the external field is much less than the probabilities of spin-lattice and cross-relaxation transitions $(W \to 0)$, the solution of (2) has the form:

$$\Delta n_{12} = A \exp(\alpha_1 t) + B \exp(\alpha_2 t) + \Delta n_{12}^0,$$

$$\Delta n_{34} = A \exp(\alpha_1 t) - \frac{B}{m} \exp(\alpha_2 t) + \Delta n_{34}^0, \tag{3}$$

where A and B are the amplitudes of the two exponentials, determined from the initial conditions

$$\alpha_1 = -1/T_1, \quad \alpha_2 = -1/T_1 - 1/T_{12},$$

$$T_{12} = m/(1 + \beta m) w'_{cr}.$$

Usually $T_{12} \ll T_1$. Hence, in Eq. (3) it is the exponential with the smaller time constant α_2 that basically characterizes the cross-relaxation. The exponential with the time constant α_1 characterizes the spin-lattice relaxation.

Let us consider a few special cases.

1. Continuous saturation of the transition 1 → 2. We have:

$$W \to \infty, \quad d\Delta n_{12}/dt = d\Delta n_{34}/dt = 0 \quad \text{whence}$$

$$\Delta n_{12} = 0, \quad (\Delta n_{34})_{\text{cont}} = \Delta n_{34}^0 \left[1 + \frac{T_1}{T_{12}} \frac{1}{1 + \beta m}\right]^{-1}. \tag{4}$$

2. Saturation by a short pulse $(\tau \ll T_{12})$. Let $\Delta n_{12} = 0$ and $\Delta n_{34} = \Delta n_{34}^0$ at $t = 0$. Then the resto-

ration of thermal equilibrium after turning off the saturating pulse is described by Eqs. (3) and the amplitudes of the exponentials have a ratio

$$B/A = \beta m. \qquad (5)$$

3. Saturation by a long pulse ($\tau \gg T_{12}$). Let $\Delta n_{12} = 0$ and $\Delta n_{34} = (\Delta n_{34})_{\text{cont}}$. The re-establishment of thermal equilibrium after the effect of the long saturating pulse will follow a relaxation curve described by Eqs. (3) with an amplitude ratio:

$$B/A = \beta m T_{12}/(T_1 + T_{12}). \qquad (6)$$

The following conclusions can be drawn from the preceding analysis. If one carries out a pulse saturation of the transition 1 ⟶ 2 and observes the restoration of the paramagnetic resonance line corresponding to this transition following the pulse, then the observed relaxation curve will be described by the sum of two exponentials, one describing the spin-lattice relaxation, and the other, much faster one the spin-spin cross-relaxation. If saturation is by a short pulse, the importance of the cross-relaxation exponential grows with an increase in the multiplicity m of the cross-relaxation transitions between the level pairs E_1, E_2 and E_3, E_4. For saturation with a long pulse the importance of the cross-relaxation exponential is reduced by a factor $(T_1 + T_2)/T_{12}$ compared with the case of a short pulse [cf. Eqs. (5) and (6)]. Note that in Eqs. (5) and (6) the parameter

$$\beta = \Delta n^0_{34}/\Delta n^0_{12} = \exp\{h(\nu_{43} - \nu_{21})/kT\}$$

depends on temperature; $\beta \approx m$ when $h\nu_{43} \ll kT$.

4. EXPERIMENTAL RESULTS AND DISCUSSION

The relaxation processes in chromium corundum were investigated in different lines at crystal trigonal axis orientations relative to the external magnetic field, θ, varying from 0 to 20°. It was found that the shape of the relaxation curves of the restoration of the intensity of the paramagnetic resonance line after the saturating pulse depended strongly on the Cr^{3+} ion concentration. Thus, for saturation by a long pulse the relaxation curves of the various transitions, for samples having concentrations 0.05, 0.4, and 0.65%, were very nearly uni-exponential, whereas for samples having concentrations 0.1 and 0.15% the relaxation curves were described in the majority of the observed transitions by a sum of two exponentials with greatly different time constants. The amplitude ratio of these exponentials depended strongly on the angle θ.

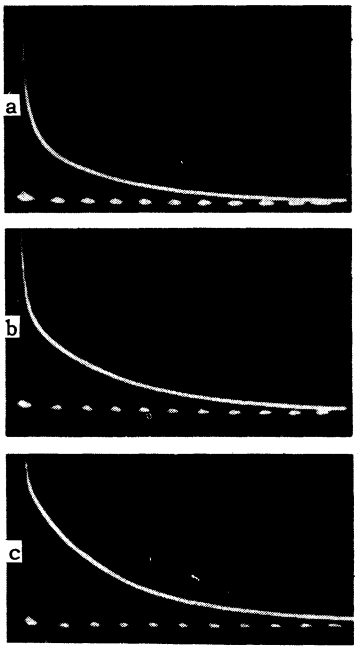

FIG. 2. Oscillograms of relaxation curves of the transition $-\frac{1}{2} \to \frac{1}{2}$ for a sample having a Cr^{3+} concentration of 0.15% for different orientations of the crystal: a) $\theta = 0°$, b) $\theta = 10°$, c) $\theta = 15°$. Duration of pulse $\tau = 220$ millisec. The time markers on the baseline are 20 millisec apart.

Figure 2 shows oscillograms of the relaxation curves for the transition $-\frac{1}{2} \to \frac{1}{2}$ at various values of θ, obtained on a sample with Cr^{3+} concentration 0.15% at T = 4.2°K. The "fast" exponentials in the relaxation curves were ascribed to the influence of spin-spin cross-relaxation.

To investigate the aforementioned effects in greater detail, experiments using different pulse lengths were tried. For short saturating pulses of length $\tau = 0.8$ millisec the importance of the "fast" exponentials increases markedly, confirming that these do characterize the cross-relaxation interaction.

Table I. Relaxation times and weight of the cross-relaxation exponential for a long saturating pulse ($\tau \gg T_{12}$) Cr^{3+} concentration 0.15%, T = 4.2°K

Transition	θ, deg	T_1, millisec	T_{12}, millisec	$B/(A+B)$, %	Transition	θ, deg	T_1, millisec	T_{12}, millisec	$B/(A+B)$, %
$-1/2 \to 1/2$	0	56.6	4.3	60	$1/2 \to 3/2$	0	46	7.8	30
$-1/2 \to 1/2$	10	56	3.7	50	$1/2 \to 3/2$	10	42	7.1	60
$-1/2 \to 1/2$	15	56	2.1	20	$1/2 \to 3/2$	15	35	6.1	77
$3/2 \to 1/2$	0	96	—	10	$-1/2 \to 3/2$	15	40	4.0	46
$3/2 \to 1/2$	15	84	—	5					

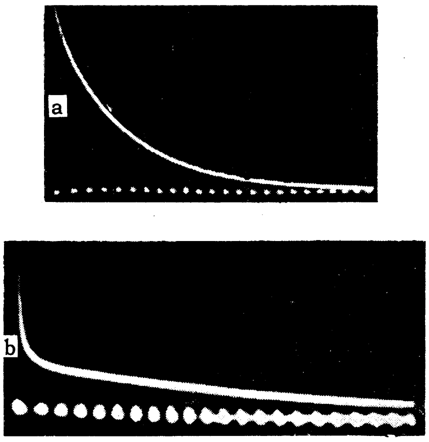

FIG. 3. Relaxation curves of the transition $^3/_2 \rightarrow ^1/_2$ ($\theta = 0°$) for different durations of the saturating pulses: a) $\tau = 460$ millisec, T = 4.2°K, b) $\tau = 0.8$ millisec, T = 1.7° K. Time markers – 20 millisec.

In order to illustrate the influence of saturating pulse length we show in Fig. 3 relaxation curves for the transition $^3/_2 \rightarrow ^1/_2$ at $\theta = 0°$ for a 0.15% sample, and for pulse lengths of 460 millisec (Fig. 3a) and 0.8 millisec (Fig. 3b). In Fig. 3b it can be seen that the relaxation curve contains two readily separable exponentials representing fast cross-relaxation and slow spin-lattice relaxation. Similar relaxation curves are also observed for the other transitions in the spectrum.

Tables I and II give the experimental data for the spin-lattice relaxation time T_1 and the spin-spin cross relaxation time T_{12}, as well as the weight of the cross-relaxation exponential $B/(A+B)$ for a 0.15% sample saturated by long and short pulses.

In Fig. 4 are shown the energy levels of Cr^{3+} in Al_2O_3 as a function of the intensity of the external magnetic field for various values of the angle θ between this field and the crystal axis. Also shown in these figures are the transitions between which cross-relaxation takes place. As can be seen from Tables I and II, cross-relaxation is most effective for transitions having a whole-number ratio of the splittings between corresponding levels.

However, cross-relaxation also takes place in the case of splittings that are not exact multiples. This leads to a superposition of the effects of cross-relaxation from several transitions. As an example, in the interval $\theta = 0$ to 15°, cross-relaxation effects between the transitions $-^1/_2 \rightarrow ^1/_2$, $-^3/_2 \rightarrow ^3/_2$ and $-^3/_2 \rightarrow -^1/_2$ are superposed. This circumstance can probably be explained by the fact that the values of T_{12} as determined with long and short saturating pulses differ from one another for the same observed transition by a factor of 1.5 to 2 (cf. Tables I and II).

The values presented in Tables I and II can be compared with the theory of cross-relaxation considered in Sec. 3. Using the experimentally determined T_1 and T_{12} one can calculate the weights of the cross-relaxation exponential from Eqs. (5) and (6). The results of such calculations for some of the transitions are presented in Table III. A comparison of the data in Tables I, II, and III shows that there is a rather good agreement between the experimental and theoretical values of the amplitudes of the cross-relaxation exponentials, particularly for the cases involving short saturating pulses.

It is interesting to note that the effects of cross-relaxation are strongly pronounced for the $^3/_2 \rightarrow ^1/_2$ transition in weak fields. For the transition at $\theta = 20°$ the weight of the cross-relaxation exponential amounts to 87% in saturation by short pulses (see Table II), which agrees with the calculated value if one assumes $m = 2$. However, it can be seen in Fig. 4d that there are no cross-relaxation transitions of multiplicity $m = 2$ for this transition. This suggests that besides the cross-relaxation interactions, between levels having a multiple ratio of splittings, considered in Sec. 3, a "combination" type of cross-relaxation interaction is also possible.

Transitions that can occur between levels by such "combination" spin-spin interactions are illustrated in Fig. 5. If the splittings of levels 1,

Table II. Relaxation times and weight of the cross-relaxation exponential for a short saturating pulse ($\tau \ll T_{12}$) Cr^{3+} concentration 0.15%

T, °K	Transition	θ, deg	T_1, millisec	T_{12}, millisec	$B/(A+B)$, %	T, °K	Transition	θ, deg	T_1, millisec	T_{12}, millisec	$B/(A+B)$, %
4.2	$-^1/_2 \rightarrow ^1/_2$	0	56.6	2,8	93	1.7	$-^1/_2 \rightarrow ^1/_2$	0	140	3.3	95
	$-^1/_2 \rightarrow ^1/_2$	10	56	2	95		$-^1/_2 \rightarrow ^1/_2$	10	140	2.8	95
	$-^1/_2 \rightarrow ^1/_2$	15	56	1	90		$-^1/_2 \rightarrow ^1/_2$	15	146	1.6	88
	$^1/_2 \rightarrow ^3/_2$	0	46	10	63		$-^1/_2 \rightarrow ^1/_2$	20	160	1,5	88
	$^1/_2 \rightarrow ^3/_2$	10	42	1.5	86		$^3/_2 \rightarrow ^1/_2$	0	344	5	69
	$^1/_2 \rightarrow ^3/_2$	15	35	5,5	90		$^3/_2 \rightarrow ^1/_2$	10	308	4	72
							$^3/_2 \rightarrow ^1/_2$	20	316	4	87

Table III

θ, deg	Observed transition	Cross-relaxation transition	Ratio of the frequencies of cross-relaxation and observed transitions, m	Calculated weights of the cross-relaxation exponentials (in %) for saturation by	
				long pulses	short pulses
0	$-{}^1/_2\to{}^1/_2$	$-{}^3/_2\to{}^3/_2$	3	45	92(T=8,2°K) 94(T=2,7°K)
10	${}^1/_2\to{}^3/_2$	$-{}^1/_2\to{}^1/_2$	2	40	82(T=4,2°K)
15	$-{}^1/_2\to{}^1/_2$	$-{}^3/_2\to-{}^1/_2$	2	15	82(T=4,2°K) 86(T=1,7°K)
15	${}^1/_2\to{}^3/_2$	$-{}^3/_2\to-{}^1/_2$	3	63	92(T=4,2°K)

Table IV. Spin-lattice relaxation times T_1 for samples of corundum of different Cr^{3+} concentration

Concentration, %	Transition	θ, deg	T_1, millisec.		Concentration, %	Transition	θ, deg	T_1, millisec.	
			T =4,2°K	T=1,7°K				T =4,2°K	T=1,7°K
0.05	$-{}^1/_2\to{}^1/_2$	0	98	200	0.1	${}^3/_2\to{}^1/_2$	0	100	290
	$-{}^1/_2\to{}^1/_2$	12	—	350		$-{}^1/_2\to{}^3/_2$	10	59	—
	${}^3/_2\to{}^1/_2$	0	208	430		$-{}^1/_2\to{}^3/_2$	15	43	130
	${}^3/_2\to{}^1/_2$	12	130	—	0.4	$-{}^1/_2\to{}^1/_2$	0	20	—
0.1	$-{}^1/_2\to{}^1/_2$	0	64	160		${}^3/_2\to{}^1/_2$	15	21	—
	$-{}^1/_2\to{}^1/_2$	10	63	145	0.65	$-{}^1/_2\to{}^1/_2$	0	1	—
	$-{}^1/_2\to{}^1/_2$	15	59	145					

2, 3, and 4 are such that $2(E_4-E_2) = 2(E_2-E_1) + (E_4-E_3)$, then cross-relaxation can occur as a result of a transition of two ions from level 4 to level 2 accompanied by the transition of two ions from level 1 to level 2 and one ion from level 3 to level 4. The total energy of the spin system is conserved in such transitions. If such "combination" processes are effective, then they can explain the cross-relaxation for the ${}^3/_2\to{}^1/_2$ transition. For this transition at $\theta = 20°$ we have the following relation between the splittings of the levels: $2(E_{1/2}-E_{3/2}) = 2(E_{-3/2}-E_{3/2}) + (E_{1/2}-E_{-1/2})$.

We shall now present the results of the investigation of relaxation in samples of corundum having Cr^{3+} concentrations of 0.05, 0.4, and 0.65%. For these samples, as we have already noted above,

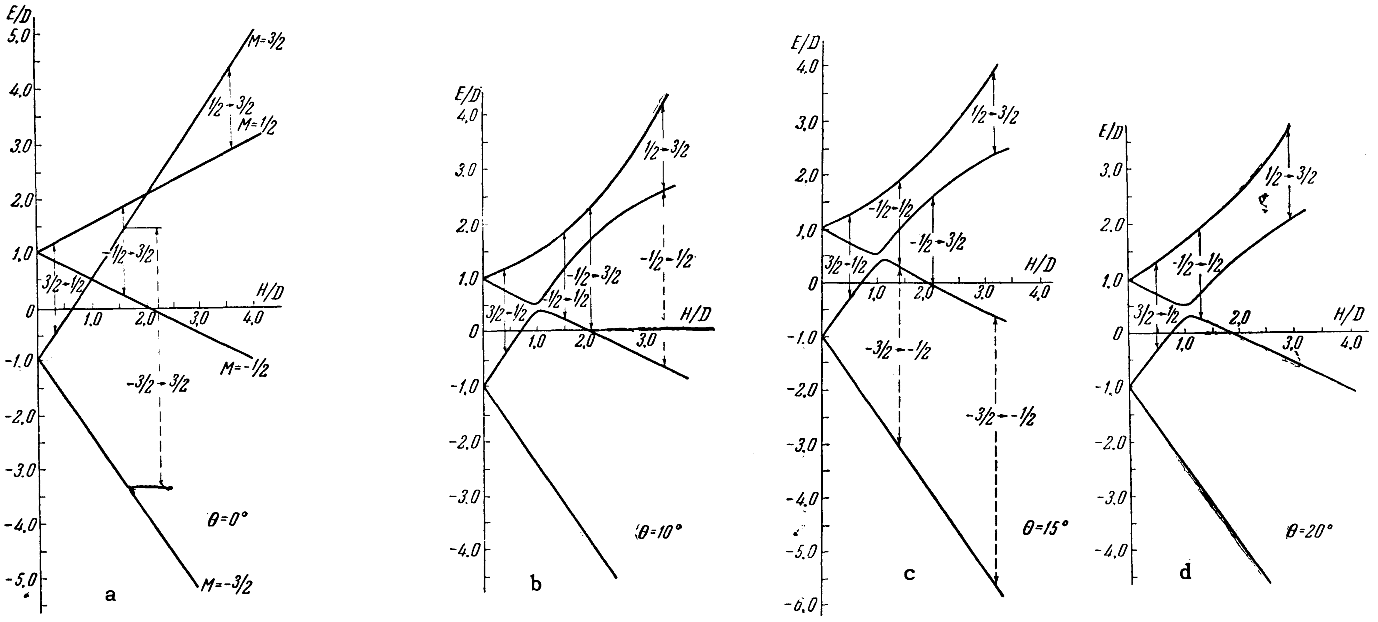

FIG. 4. Energy levels of Cr^{3+} in Al_2O_3 as a function of the applied magnetic field intensity H for different values of the angle θ. D is the crystalline field parameter. The arrows indicate transitions: solid – observed at 9400 Mc, dashed – cross-relaxation.

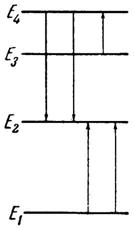

FIG. 5. Transitions for cross-relaxation processes of the "combination" type.

the observed relaxation curves are very nearly uni-exponential and correspond to spin-lattice relaxation. The relaxation times determined by long-pulse saturation are presented in Table IV. Also shown are the values of T_1 for a 0.1% sample. It can be seen from Table IV that the spin-lattice relaxation times at helium temperatures depend strongly on the Cr^{3+} ion concentration. This fact was established earlier by us[4] and was later confirmed in papers by Pace et al[6] and by Zverev.[10] It has been theoretically discussed on the basis of an assumption of the effect of defects in the crystalline lattice.[2] It is also possible that the concentration dependence of the spin-lattice relaxation time in chromium corundum is caused by exchange interactions between Cr^{3+} ions.[10] The fact that the paramagnetic resonance line width of Cr^{3+} in Al_2O_3 is not explainable by the theory of dipole broadening[12] is possibly connected with the presence of exchange interactions. The temperature dependence of T_1 in the interval 4.2—1.7°K follows the law $T_1 \sim T^{-1}$ within the limits of experimental error (~ 10—15%), and this indicates that the spin-lattice relaxation at helium temperatures occurs as the result of direct one-phonon processes. 12

We might remark that the discrepancy at high concentrations between the values for T_1 presented here, which were determined by the pulse saturation method, and the values of T_1 we obtained earlier from experiments using continuous saturation,[4] is attributable to the influence of cross-relaxation. At low concentrations, where the cross-relaxation interactions are not effective, both methods give close values for T_1.

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Translated by L. M. Matarrese