SOVIET PHYSICS JETP VOLUME 13, NUMBER 6 DECEMBER, 1961

ELECTRONIC PARAMAGNETIC RESONANCE OF THE Fe^{3+} *ION IN CORUNDUM*

L. S. KORNIENKO and A. M. PROKHOROV

Institute of Nuclear Physics, Moscow State University

Submitted to JETP editor January 4, 1961

J. Exptl. Theoret. Phys. (U.S.S.R.) **40**, 1594-1601 (June, 1961)

Results are presented of an experimental study at various temperatures (290, 77, and 4.2°K) of the electronic paramagnetic resonance of the Fe^{3+} ion in corundum. Spin lattice relaxation times were measured at 4.2°K. The constants of the spin Hamiltonian and their temperature variation were determined.

THE electronic paramagnetic resonance (e.p.r.) spectrum of the Fe^{3+} ion in corundum was first studied by the authors in 1957.[1] It was shown subsequently[2] that this material can be used to make a paramagnetic amplifier. This served as one of the reasons for a more detailed study of the Fe^{3+} ion e.p.r. in corundum.

As is well known, the ground state of the Fe^{3+} ion is a ^6S-state with electronic configuration of the unfilled shell $3d^5$. Since the orbital momentum is zero in this case, to explain the existence of fine structure in the e.p.r. spectrum we must consider, apart from the ground state, higher impurity energy states, corresponding to other electronic configurations. The mechanism that gives rise to the splitting of the ^6S ground state has been discussed theoretically by a number of authors,[3-7] who have analyzed the various types of high-order perturbations, taking into account the effect of the electrostatic field of the crystal, spin-orbit coupling, and magnetic spin-spin interaction.

The investigations we previously made[1] in the frequency range 25 — 40 kMc enabled the form of the spin Hamiltonian and the values of its constants to be determined at room temperature (290° K) for a paramagnetic ion concentration (Fe:Al) of 0.01 — 0.02% (and not 0.1%, as was erroneously stated in reference 1). We have also reported[2] that the constant D is positive. This was established by comparing the relative intensities of the e.p.r. lines at 290 and 4.2°K. The experiments referred to were made at a wavelength of about 0.8 cm. From the fact that the sign of the constant a − F is the same as that of the constant D, it follows that it, too, is positive.

In the present paper the results are given of more accurate measurements of the e.p.r. spectra for the cases when the trigonal axis of the crystal is parallel or perpendicular to the direction of the external magnetic field (for brevity we will call these the parallel and perpendicular orientations); the measurements were made at frequencies in the range 9 — 10 kMc at temperatures of 290, 77, 4.2 and 2° K. From these measurements the values of the spin Hamiltonian constants were found at the various temperatures. Direct measurements were also undertaken of the initial splitting of the ground state energy levels (in zero magnetic field) at temperatures of 290 and 4.2° K, and of the spin-lattice relaxation time τ_1 at 4.2° K. The paramagnetic ion concentration in the specimens studied was 0.02 and 0.002%.

As was shown in reference 1, the e.p.r. spectrum of the Fe^{3+} ion in corundum can be interpreted with the aid of the spin Hamiltonian:[8]

$$\begin{aligned}\hat{\mathcal{H}} = {} & g\beta\mathbf{H}\hat{\mathbf{S}} + D\left[\hat{S}_z^2 - \tfrac{1}{3}S(S+1)\right] + \tfrac{1}{6}a\left[\hat{S}_\xi^4 + \hat{S}_\eta^4 + \hat{S}_\zeta^4 \right. \\ & \left. - \tfrac{1}{5}S(S+1)(3S^2+3S-1)\right] \\ & + \tfrac{1}{180}F\left[35\hat{S}_z^4 - 30S(S+1)\hat{S}_z^2 + 25\hat{S}_z^2 - 6S(S+1)\right. \\ & \left. + 3S^2(S+1)^2\right], \qquad (1)\end{aligned}$$

where g is the spectroscopic splitting factor, assumed isotropic, β is the Bohr magneton, **H** is the vector magnetic field strength, $\hat{\mathbf{S}}$ is the electronic spin operator ($\hat{S}_i$ is the operator projecting it on the corresponding axis) with eigenvalue $S = 5/2$, a is the constant of the cubic crystal field, D and F are the constants of the trigonal crystal field of the second and fourth order, respectively. The coordinate system $\xi\eta\zeta$ lies along the cubic axes of the crystal field, and the z axis is directed along the trigonal axis of the crystal, which is also the [111] axis of the system $\xi\eta\zeta$.

When the Fe^{3+} ion replaces the Al^{3+} ion isomorphously in the crystalline lattice of corundum, there are two nonequivalent cases, differing in the directions of the cubic axes of the crystal field. The three cubic axes of one type of ion can be ob-

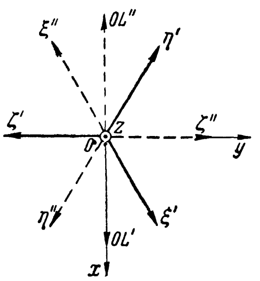

FIG. 1. The coordinate axes used in the expressions for the spin Hamiltonian of the Fe^{3+} ion in corundum. $\xi'\eta'\zeta'$ and $\xi''\eta''\zeta''$ are the projections of the mutually perpendicular axes of the cubic crystal field for the first and second systems of non-equivalent ions, respectively. (The axes themselves are inclined upwards.) z is the axis of the trigonal crystal field (directed vertically upwards). The x axis bisects the angle between the projections of the cubic axes ξ' and η''. OL$'$ and OL$''$ are lines used for calculating the Euler angles φ_1 and φ_2 for the first and second system of ions, respectively.

tained by reflecting the corresponding three axes of the other type of ion in the plane perpendicular to the trigonal axis (xy), or by rotating it through 60°. When the axes are labelled as in Fig. 1, the Euler angles for transforming from the coordinates xyz to the coordinates $\xi\eta\zeta$ are, for the first system ($\xi'\eta'\zeta'$),

$$\varphi_1 = 0,\ \theta = 54°44',\ \varphi_2 = 45°,$$

and for the second system ($\xi''\eta''\zeta''$)

$$\varphi_1 = 180°,\ \theta = 54°44',\ \varphi_2 = 45°.$$

After introducing the dimensionless coefficients

$$\begin{aligned} h_i &= g\beta H_i/D \quad (i = x, y, z), \\ \alpha &= a/D, \\ f &= F/D, \end{aligned} \tag{2}$$

substituting S = $^5/_2$ in (1), and, for simplicity, changing $S(S+1)/3 = {}^{35}/_{12}$ into $^5/_4$ (this changes the Hamiltonian trivially by a constant), and after the necessary transformations, we obtain, in the representation that makes the matrix operator $\hat{S}_z$ diagonal, the Hamiltonian matrix for the Fe^{3+} ion in corundum in the following form:

$$\left\| \begin{matrix} -\frac{5}{2}h_z+5-\frac{\gamma}{3} & \frac{\sqrt{5}}{2}h^+ & 0 & \pm ip & 0 & 0 \\ \frac{\sqrt{5}}{2}h^- & -\frac{3}{2}h_z+1+\gamma & \sqrt{2}\,h^+ & 0 & 0 & 0 \\ 0 & \sqrt{2}\,h^- & -\frac{1}{2}h_z-1-\frac{2\gamma}{3} & \frac{3}{2}h^+ & 0 & \mp ip \\ \mp ip & 0 & \frac{3}{2}h^- & \frac{1}{2}h_z-1-\frac{2\gamma}{3} & \sqrt{2}\,h^+ & 0 \\ 0 & 0 & 0 & \sqrt{2}\,h^- & \frac{3}{2}h_z+1+\gamma & \frac{\sqrt{5}}{2}h^+ \\ 0 & 0 & \pm ip & 0 & \frac{\sqrt{5}}{3}h^- & \frac{5}{2}h_z+5-\frac{\gamma}{3} \end{matrix} \right\| \tag{3}$$

$$h^{\pm} = h_x \pm ih_y, \qquad \gamma = \alpha - f, \qquad p = (2\sqrt{5}/3)\alpha.$$

For the matrix elements with plus-or-minus sign, the upper sign corresponds to the first, and the lower sign to the second system of non-equivalent ions. Inspection of the matrix (3) shows that the constant f is present only in the combination ($\alpha - f$) with the constant α. The constant α also appears in terms with plus-or-minus signs, and, on changing the sign of α, the Hamiltonian matrix for one system of ions transforms into the matrix for the other system. Since it is impossible to establish which of the two experimentally observed spectra corresponds to which system of ions, it follows that by measuring the positions of the e.p.r. lines it is impossible to determine either the value of the constant f (except in the combination $\alpha - f$), or the sign of the constant α.

For the parallel orientation ($h_z = h$, $h_x = h_y = 0$), the sixth-degree secular equations for both systems of ions are equivalent, and can be factored into two linear and two quadratic equations. In this case the energy levels depend on the value of the external magnetic field h as follows:

$$\begin{aligned} \varepsilon_{6,3} &= +h + 2 - \tfrac{1}{2}(\alpha - f) \\ &\pm \tfrac{1}{6}\sqrt{\{9h + [18 + (\alpha - f)]\}^2 + 80\alpha^2}, \\ \varepsilon_{5,2} &= \pm\tfrac{3}{2}h + 1 + (\alpha - f), \\ \varepsilon_{4,1} &= -h + 2 - \tfrac{1}{2}(\alpha - f) \\ &\pm \tfrac{1}{6}\sqrt{\{9h - [18 + (\alpha - f)]\}^2 + 80\alpha^2}. \end{aligned} \tag{4}$$

The energy levels are numbered in order of increasing energy in strong magnetic fields. The

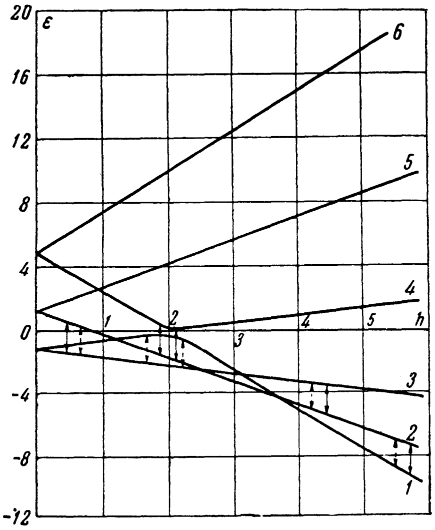

FIG. 2. The variation of the energy levels of the Fe^{3+} ion in corundum with the magnetic field for the parallel orientation ($\theta = 0°$). The arrows indicate the resonance transitions when radiation with frequencies in the range 9 – 10 kMc is used (full arrows for the case $\nu > \nu''$, broken arrows for the case $\nu < \nu'$). The numbers on the curves give the numbers of the levels in order of increasing energy in strong magnetic fields. The axes are marked in dimensionless units: $\varepsilon = E/D$, where E is the energy of the level; $h = g\beta H/D$.

variation of the position of the energy levels with the magnetic field h is shown in Fig. 2.*

The wave functions φ_i of the corresponding energy levels ϵ_i can be expanded in terms of the eigenfunctions ψ_k of the operator $\hat{S}_z$, where k = 1, 2, ... 6 corresponds to its eigenvalues with M $= -5/2, -3/2, \ldots, +5/2$:

$$\varphi_1 = \alpha_1\psi_1 + i\alpha_2\psi_4, \quad \varphi_2 = \psi_2, \quad \varphi_3 = \beta_1\psi_3 + i\beta_2\psi_6,$$
$$\varphi_4 = i\alpha_2\psi_1 - \alpha_1\psi_4, \quad \varphi_5 = \psi_5, \quad \varphi_6 = i\beta_2\psi_3 - \beta_1\psi_6. \qquad (5)$$

Here

$$\alpha_1 = (a_{44} - \varepsilon_1)/\sqrt{(a_{44} - \varepsilon_1)^2 - p^2},$$
$$\alpha_2 = p/\sqrt{(a_{44} - \varepsilon_1)^2 - p^2},$$
$$\beta_1 = (a_{66} - \varepsilon_3)/\sqrt{(a_{66} - \varepsilon_3)^2 - p^2},$$
$$\beta_2 = p/\sqrt{(a_{66} - \varepsilon_3)^2 - p^2};$$

a_{ii} are the corresponding diagonal terms in (3), and $p = (2\sqrt{5}/3)\,|\alpha|$.

When radiation with a frequency in the range 9 – 10 kMc is used, five e.p.r. lines can be observed. The first, fourth, and fifth (in order of increasing value of the magnetic field at resonance) correspond to transitions 3 ⟷ 2, 2 ⟷ 3 and 1 ⟷ 2 (the first number is the number of the lower level, and the second, the number of the upper level). For frequencies $\nu < \nu'$ the second and third lines correspond to the transition 3 ⟷ 1, but for frequencies $\nu > \nu''$ they correspond to the transition 2 ⟷ 4. The frequencies ν' and ν'' are certain critical frequencies, the values of which depend on temperature, as do the values of the spin Hamiltonian constants. If $\nu' < \nu < \nu''$, the second and third lines are generally not observed. The values of ν' and ν'' can be calculated, if the values of the spin Hamiltonian constants are known, from the condition $\partial(\Delta\epsilon)/\partial h = 0$, where $\Delta\epsilon$ is the energy difference between the first and third, or fourth and second levels. These conditions result in the expressions

$$h\nu' \approx 2D + \tfrac{1}{9}(a - F) - \tfrac{4}{9}\sqrt{10}\,|a| + \tfrac{5}{27}|a|^2/D, \qquad (6)$$

$$h\nu'' = 2D - \tfrac{13}{9}(a - F) + \tfrac{4}{9}\sqrt{10}\,|a|. \qquad (7)$$

As can be seen from (6) and (7), if frequencies are used which are close to ν' or ν'' (but do not lie between them), it is possible to determine the value of |a| from terms of the same order of magnitude as the terms which contain a – F (we recall that in reference 1 the value of |a| was found from terms which were second order perturbations, and this led to a lower accuracy). This fact was taken into account when the frequencies used in the study of the e.p.r. spectrum were chosen.

The e.p.r. lines were observed with the aid of a reflection type radiospectrometer. Accurate orientation of the crystal relative to the direction of the external magnetic field was obtained with a resonator of special construction, which allowed the crystal to be rotated about two mutually perpendicular axes in the course of the experiment. The frequency of the microwave source was stabilized with respect to the spectrometer resonator; the absolute frequency error was continuously controlled, and did not exceed 0.2 – 0.3 Mc. To measure the magnetic field strength proton nuclear magnetic resonance was used. The diameter of the pole pieces of the electromagnet used in the experiments was 260 mm, and the distance between the pole pieces was 30 – 65 mm. To increase the accuracy of measurement, the distribution of the magnetic field in the gap between the poles was explored, and the paramagnetic crystal and proton transducer of the field measuring device were placed at points whose field values differed by less than 0.005%.

It was established in the course of the experiments that, when working at frequencies such that $\nu > \nu''$, an operating frequency could be chosen closer to the critical frequency than when working

---

*The solution of the secular equation in this case has also been considered by Vinokurov, Zaripov, and Yafaev.[9]

Table I

Temperature, °K	Frequencies Mc	Resonance magnetic field values (oe) corresponding to various transitions				
		$3 \longleftrightarrow 2$	$2 \longleftrightarrow 4$	$2 \longleftrightarrow 4$	$2 \longleftrightarrow 3$	$1 \longleftrightarrow 2$
290	9641.7	752.5	3489.3	3595.6	7624.8	10147.2
		(752.5) *	(3490.5)	(3595.3)	(7624.6)	(10146.8)
77	9838.4	778.8	3589.3	3658.5	7789.9	10363.1
		(778.7)	(3587.7)	(3657.6)	(7789.7)	(10363.0)
4.2	9846.8	779.4	3592.8	3663.0	7798.0	10375.5
		(779.8)	(3592.5)	(3662.5)	(7798.0)	(10375.7)

*In brackets are given the values calculated from the spin Hamiltonian constants given in Table II.

Table II

Constants	Values of the spin Hamiltonian constants for the Fe^{3+} ion* in corundum		
	at 290°K	at 77°K	at 4.2°K
g	2.0030 ± 0.0006	2.0032 ± 0.0007	2.0029 ± 0.0007
D, Oe	$+1796.4 \pm 0.4$	$+1836.2 \pm 0.6$	$+1838.5 \pm 0.6$
$a - F$, Oe	$+353.2 \pm 0.4$	$+362.6 \pm 0.5$	$+362.7 \pm 0.5$
$\|a\|$, Oe	248.7 ± 1.0	254.1 ± 1.3	253.5 ± 1.3

*Fe^{3+} ion concentration $\leq$ 0.02%.

at frequencies such that $\nu < \nu'$. When the frequency approached the critical value ν', the e.p.r. lines corresponding to the transition $1 \longleftrightarrow 3$ smeared out more rapidly than the lines corresponding to the transition $4 \longleftrightarrow 2$ when the other critical frequency ν'' was approached. Since the values of the spin-Hamiltonian constants, and, consequently, the quantities ν' and ν'', depended on temperature, the radiation frequency used in the experiments at various temperatures also varied. The frequencies lay in the range 9000 — 9200 Mc ($\nu < \nu'$), and 9600 — 9850 Mc ($\nu > \nu''$).

In Table I a summary is presented of the experimental data on the positions of the e.p.r. line peaks in the magnetic field for the parallel orientation, measured at frequencies $\nu > \nu''$ and at different temperatures, for specimens with 0.02% Fe^{3+} ion concentration. For comparison, the brackets contain the values of the resonance fields calculated on the basis of the spin-Hamiltonian constants found from these measurements and given in Table II. Measurements made at frequencies $\nu < \nu'$ gave results in agreement with measurements at $\nu > \nu''$.

The width of the first, fourth and fifth lines, measured between the half-intensity points, was 10 ± 2 oe for the specified paramagnetic ion concentration, and did not depend on temperature. The widths of the second and third lines depend greatly on the radiation frequency chosen, since the corresponding transitions occur in a region where the derivative $\partial\epsilon/\partial h$ for the fourth or third levels changes sign. Usually the quantity $\Delta\nu = \nu - \nu''$ ($\nu' - \nu$) was chosen, so that the width of these lines was 20 — 30 oe.

Measurements at a temperature of about 2°K showed that the values of the spin-Hamiltonian constants at this temperature did not differ from the values at 4.2°K.

At 290°K measurements were also made of the e.p.r. spectra for the parallel orientation on specimens with paramagnetic ion concentrations of 0.002%. These measurements showed that the possible deviation of the constants from the values given in Table II does not exceed the limits of experimental error. The line width in this case is 10 — 20% smaller than when the concentration is 0.02%. This shows that magnetic dipole-dipole interaction of the paramagnetic ions is already starting to have a significant effect in the range of concentrations considered.

The shape of the lines is intermediate between Gaussian and Lorentzian, and its character does not change in this concentration range. When the concentration of the Fe^{3+} ions is further diminished, the widths of the e.p.r. lines remain practically unchanged.

It is seen from our results that the values of the constants D, a − F, and | a |, all increase as the temperature is lowered, but that the value of the constant g is practically unchanged. The values obtained for the constants agree with the results of Bogle and Simmons,[10] with the exception of the constant | a |, which they found to get

Table III

Temperature, °K	Experimental value of hν/D	Resonance magnetic field value (oe)	Calculated value of hν/D	$\left\lvert\frac{h\nu_{\text{exp.}}-h\nu_{\text{calc.}}}{h\nu_{\text{exp.}}}\right\rvert$, %
290	1.9138 (ν=9640.5 Mc)	1355.4 3394.9 7294.0	1.9138 1,9139 1.9168	— 0,005 0.15
77	1.9109 (ν=9838.5 Mc)	1381.1 3467.6 7445.6	1.9097 1.9107 1.9115	0.06 0.01 0.03
4.2	1.9105 (ν=9846.6 Mc)	1383.8 3470.2 7456.3	1,9106 1.9099 1.9126	0.005 0.03 0,1

smaller as the temperature was decreased. They obtained this result, apparently, because the crystal was not oriented sufficiently accurately.

For the perpendicular orientation of the crystal ($h_x = h$, $h_z = h_y = 0$), the sixth order secular determinant for the energy levels can be written as the product of two third order determinants: $\Delta = \Delta_+\Delta_- = 0$, where

$$\Delta_{\pm} = \begin{vmatrix} 5-\frac{1}{3}(\alpha-f)-\varepsilon & \frac{\sqrt{5}}{2}h & +i\frac{2\sqrt{5}}{3}\lvert\alpha\rvert \\ \frac{\sqrt{5}}{2}h & 1+(\alpha-f)-\varepsilon & \sqrt{2}\,h \\ -i\frac{2\sqrt{5}}{3}\lvert\alpha\rvert & \sqrt{2}\,h & -1-\frac{2}{3}(\alpha-f)\pm\frac{3}{2}h-\varepsilon \end{vmatrix}. \tag{8}$$

Analysis of the secular equation shows that the energy spectrum does not change when the crystal is rotated about the trigonal axis while this remains perpendicular to the direction of the magnetic field. This prediction agrees with experiment.

The behavior of the energy levels for the perpendicular orientation is shown in Fig. 3. Three e.p.r. lines are observed in this case, to which are added two other lines for some radiation frequency values; the latter two lines correspond to transitions between levels 2 and 3 (they are shown in Fig. 3 by broken arrows). It was ascertained how well the spectrum for the perpendicular orientation could be described by the spin Hamiltonian (1) with the values of the constants found from the spectrum in the parallel orientation. To do this, the energy difference of the levels between which the corresponding resonance transition occurs was calculated, using the values for the constants from Table II, for each of the experimental values of the resonance magnetic field. The value obtained was compared with the quantum of radiation used. The results of this comparison are given in Table III.

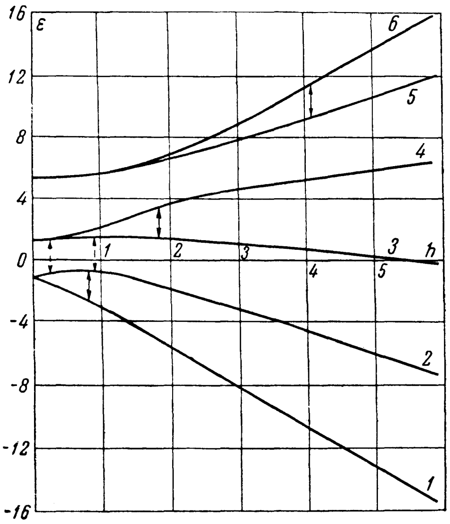

FIG. 3. Variation of the energy levels of the Fe^{3+} ion in corundum with the magnetic field for the perpendicular orientation ($\theta = 90°$).

Direct measurements were also made on the initial splitting (in the absence of magnetic field) between the neighbors of the spin doublets in the ^6S ground state at 290 and 4.2° K. The following results were obtained:

	$T = 290°$ K	$T = 4.2°$ K
Δ_1, Mc:	11768±4 (11759±6)	12046±13 (12044±6)
Δ_2, Mc:	18873±11 (18866±6)	19298± 3 (19291±6),

where Δ_1 is the energy difference between the middle and lower doublets, and Δ_2 is the energy difference between the middle and upper doublets. For comparison are given in brackets the values of Δ_1 and Δ_2 calculated from the spin Hamiltonian constants (see Table II) by the formula obtained from (6) when h = 0:

$$\Delta_{2,1} = \sqrt{[3D+\tfrac{1}{6}(a-F)]^2+\tfrac{20}{9}a^2}\pm[D-\tfrac{3}{2}(a-F)]. \tag{9}$$

The agreement between the experimental and calculated values indicates that the spin Hamiltonian (1) also describes well the energy levels of the Fe^{3+} ion in corundum when the value of the external magnetic field tends to zero.

Preliminary experiments made at 290° K on specimens with Fe^{3+} ion concentrations of about

0.2 and 0.5% showed that in this case a marked dependence is observed of the spin-Hamiltonian constants on the paramagnetic ion concentration.

The method of pulse saturation was used to measure the values of the spin-lattice relaxation times τ_1 at 4.2° K. The measurements were made at a wavelength of 3.2 cm. The transition corresponding to the first e.p.r. line in the parallel orientation was studied. The time τ_1 was $(12 \pm 1) \times 10^{-3}$ sec for an Fe^{3+} ion concentration of 0.002%, and $(8 \pm 1) \times 10^{-3}$ sec for a concentration of 0.02%. The relaxation process in both cases was described by a single exponential.

The authors thank R. P. Bashuk and A. S. Bebchuk for providing the specimens for the studies, the late G. A. Feshchenko for fruitful discussions, and V. A. Kozlov and N. G. Slovetskaya for help with the measurements.

---

[1] L. S. Kornienko and A. M. Prokhorov, JETP **33**, 805 (1957), Soviet Physics JETP **6**, 620 (1958).

[2] L. S. Kornienko and A. M. Prokhorov, JETP **36**, 919 (1959), Soviet Phys. JETP **9**, 649 (1959).

[3] J. H. Van Vleck and W. G. Penney, Phil. Mag. **17**, 961 (1934).

[4] M. H. L. Pryce, Phys. Rev. **80**, 1107 (1950).

[5] Nagamija, Yosida, and Kubo, Phil. Mag. Suppl. **4**, 1 (1955).

[6] H. Watanabe, Progr. Theor. Phys. Japan **18**, 405 (1957).

[7] Powell, Gabriel, and Johnston, Phys. Rev. Letters **5**, 145 (1960).

[8] B. Bleaney and R. S. Trenam, Proc. Roy. Soc. **A223**, 1 (1954).

[9] Vinokurov, Zaripov, and Yafaev, JETP **37**, 312 (1959), Soviet Phys. JETP **10**, 220 (1960).

[10] G. S. Bogle and H. F. Symmons, Proc. Phys. Soc. **73**, 531 (1959).

Translated by K. F. Hulme
273