PHYSICAL REVIEW VOLUME 125, NUMBER 5 MARCH 1, 1962

Problem of Anomalous Resistivity in Plutonium*

R. Smoluchowski
Princeton University, Princeton, New Jersey and Los Alamos Scientific Laboratory, Los Alamos, New Mexico

(Received October 26, 1961)

The anomalous resistivity of plutonium is interpreted in terms of interband scattering. It is shown that a reasonable band structure can account for the observed resistivities in alpha and in (stabilized) delta plutonium. The behavior of the anomaly as function of alloying additions is also understandable.

I. INTRODUCTION

It is well known that the monoclinic α-Pu and the face-centered (stabilized) cubic δ-Pu alloys show a similar resistivity anomaly. This is illustrated in Fig. 1 for α-Pu.[1–4] Figures 2–4 show the residual resistivity ρ_0, the difference between the maximum resistivity $\rho_{\max}$ and ρ_0, and the temperature $T_{\max}$ at which the maximum occurs as a function of alloying content in δ-Pu.[1–4] It is interesting to note that the volume per atom in the two forms of plutonium differs by about 20%, the monoclinic phase being the most dense. It is here assumed that the deviations from an ideal cubic close-packed structure, which have been proposed[5] in order to explain the negative thermal expansion coefficient of pure δ-Pu are, if real, too small to play a role in the considerations which follow. In any case most of the δ-Pu alloys here considered have a normal positive thermal expansion.

Seemingly analogous resistivity anomalies have been observed in systems which show either an atomic or an electronic order-disorder transition. Since the resistivity shows no hysteresis at low temperatures, a change of the atomic order is most unlikely unless in both phases the atomic mobility is abnormally high. On the other hand, an antiferromagnetic → paramagnetic transformation is a possibility. This kind of reasoning has been pursued particularly by Friedel who applied the

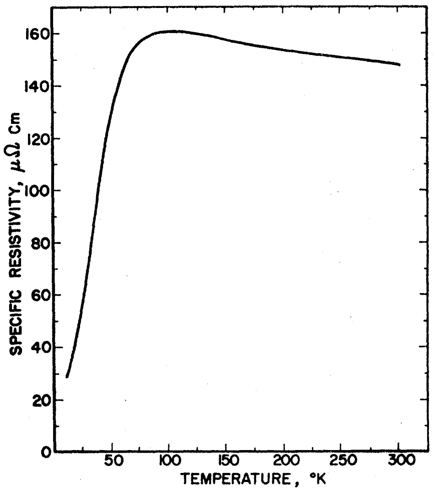


FIG. 1. Resistivity of alpha plutonium.

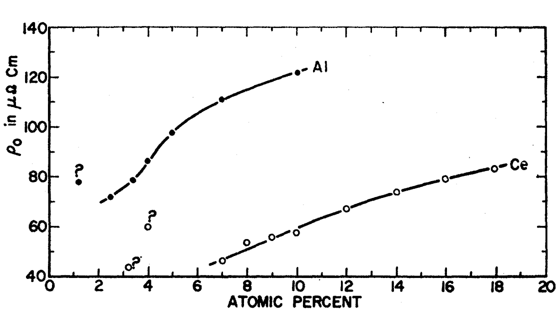


FIG. 2. Residual resistivity of delta plutonium as function of aluminum and cerium content.

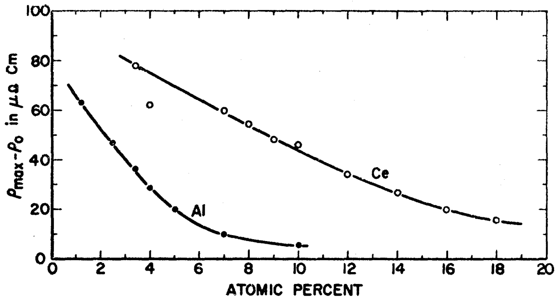


FIG. 3. Resistivity at maximum minus residual resistivity of delta plutonium as function of aluminum and cerium content.

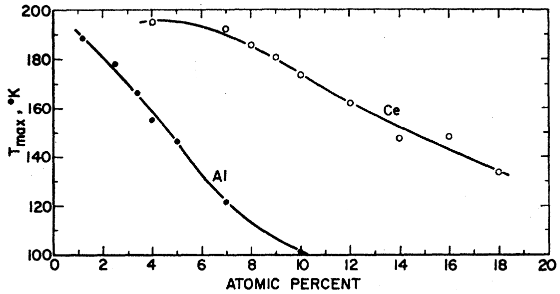


FIG. 4. Temperature at maximum resistivity of delta plutonium as function of aluminum and cerium content.

---

* Sponsored by the U. S. Atomic Energy Commission.

[1] R. O. Elliott and C. E. Olsen (to be published).

[2] J. A. Lee, G. T. Meadon, R. O. A. Hall, and E. King, International Conference on Metallurgy of Plutonium, Grenoble, 1960 (unpublished), Report No. 4.

[3] J. A. Lee, G. T. Meadon, and K. Mendelssohn, Cryogenics **1**, 52 (1960).

[4] T. A. Sandenaw, J. Phys. Chem. Solids **16**, 329 (1960).

[5] S. T. Konobeevsky and N. T. Chebotarev, Atomnaia Energiia **10**, 50 (1961).

quantitative formalism derived by him and de Gennes[6] and by Rocher.[7] [8] They conclude that there is about one conduction electron per plutonium atom in δ-Pu and that the anomalous resistivity is due to its interaction with the magnetic electrons. The high electronic specific heat and the high magnetic susceptibility point to the presence of a high density of electrons at the Fermi level. Rocher concludes in addition that an aluminum atom produces an antiferromagnetic coupling between two neighboring diametrically opposite plutonium atoms in δ-Pu. This accounts supposedly for the increased ratio of the resistivity due to magnetic scattering at the Néel point to the same resistivity for a completely disordered magnetic state. It should be kept in mind that the quantitative conclusions are based on a highly uncertain subtraction of the "normal" resistivity due to lattice vibrations from the total resistivity. In particular the essential estimate of the incoherent magnetic scattering, which is obtainable only from high-temperature data, is beset by a huge error.

In spite of these uncertainties the assumption of an antiferromagnetic model of the resistivity anomaly would be attractive were it not for the absence of other confirming observations. It is now well established[9] that the paramagnetic susceptibility of alpha plutonium is constant from 150 to 300°K. At lower temperatures it shows a slight gradual increase reaching a weak (8%) maximum near 15°K but, within a few percent accuracy, giving no indication of a Néel point near 100°K. In stabilized delta plutonium no detailed measurements of susceptibility are available but a rough estimate[2] points to a paramagnetic behavior made up of a temperature-independent and a temperature-dependent part. On the other hand neutron diffraction data[10] made on Pu-Al alloys show an absence of magnetic superlattice lines to within a few percent of the intensity of the normal reflections. There is also little evidence[11] for any specific heat anomaly in high-purity plutonium which could be definitely connected with a Néel temperature. The various irregularities sometimes observed are quite likely associated with the annealing of self-irradiation effects. One might speculate of course that the magnetic moment of Pu atom is very small since the magnetic moments of[12] $PuGe_2$ and of[13] PuH_2 are only 0.144 and about 0.2 Bohr magneton, respectively. Thus, an anomaly in susceptibility, neutron diffraction, or specific heat would not be observable. This leads, however, to obvious difficulties in accounting for the huge resistivity effect.

II. BAND STRUCTURE

In view of the above, admittedly rather unsatisfactory, situation it seems reasonable to pursue the other possible model based on interband scattering. As is well known, Mott[14] has suggested that considerable additional resistivity can be caused by such a scattering if there is a big difference in the effective mass or in the density of states at the Fermi level ζ in two (or more) bands. For a model consisting of one broad and one narrow band and with several simplifying assumptions, the temperature dependence of the Fermi level

$$\zeta=\zeta_0-\tfrac{1}{6}\pi^2(kT)^2(1/N)(dN/dE)_{\zeta 0} \tag{1}$$

leads[15] to

$$\rho(\zeta,T)=\rho(\zeta_0,T)\times\left\{1-\frac{\pi^2}{6}(kT)^2\left[\frac{-1}{N}\frac{d^2N}{dE^2}+3\left(\frac{1}{N}\frac{dN}{dE}\right)^2\right]\right\}, \tag{2}$$

at not too low temperatures. Here $N(E)$ is the density of electronic states in the band with the high effective mass. Clearly $\rho(\zeta_0,T)$, which is the resistivity which would be observed if the narrow band were also flat, is a linear function of temperature (apart from a small correction for lattice expansion). If the expression in the square brackets has a value between $2(\pi Tk)^{-2}$ and $6(\pi Tk)^{-2}$, then the resistivity is positive and its temperature derivative is negative. This puts a limit on its value between a few hundred and a few thousand $(\text{ev})^{-2}$. It is difficult to make a good estimate of the two terms in the square bracket. The best one can do is to use the approximation[16]

$$(1/N)(dN/dE)\cong 3eS/\pi^2k^2T, \tag{3}$$

where S is the absolute thermoelectric power. It should be pointed out, however, that recently[17] serious doubt has been cast on the validity of the theory which underlies the derivation of Eq. (3), especially for alloys. Experimental values[2] of S, both for α and δ (stabilized) plutonium, are positive and of the order of 10 μv deg^{-1} at low temperatures. As pointed out by Friedel, this indicates that dN/dE is positive at the Fermi level. The magnitude of S, however, is much too small to account for the required value of the square bracket. One concludes thus that the term $(1/N)(d^2N/dE^2)$ has to be large and negative.

The next step is to make a reasonable assumption as to the nature of the narrow band. Lee and Hall,[18]

---

[6] P. G. deGennes and J. Friedel, J. Phys. Chem. Solids 4, 71 (1958).

[7] Y. A. Rocher and J. Friedel, J. Phys. Chem. Solids 18, 196 (1961).

[8] Y. A. Rocher, J. Phys. Chem. Solids (to be published).

[9] See for instance, E. Grison, Mem. Sci. Rev. Met. 58, 1 (1961).

[10] K. A. Gschneidner, Jr., G. P. Arnold, N. G. Nerenson, and R. B. Roof (to be published).

[11] T. A. Sandenaw (to be published).

[12] C. E. Olsen, Suppl. J. Appl. Phys. **31**, 340S (1960).

[13] C. E. Olsen, T. A. Sandenaw, and B. T. Matthias (to be published).

[14] N. F. Mott, Proc. Roy. Soc. (London) **A153**, 699 (1936).

[15] H. Jones, *Handbuch der physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 19, p. 227.

[16] J. Friedel, J. Phys. Chem. Solids **1**, 175 (1956).

[17] C. A. Domenicali, Phys. Rev. **117**, 984 (1960).

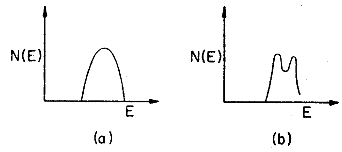
[18] J. A. Lee and R. O. A. Hall, J. Less Common Metals **1**, 356 (1959).

using the analogy to Ridley's[19] and Lehman's[20] calculations (for uranium) which showed that the 7*s* band is empty (or nearly so), conclude that the conduction band in plutonium is 6*d* and the narrow band is 5*f*. Friedel on the other hand leans toward a 7*s* conduction band and a mixed 6*d*-5*f* narrow band. For simplicity let us follow Lee and Hall's model and assume further that the band has a parabolic shape as illustrated in Fig. 5(a). This gives the right sign to the second derivative of $N(E)$. Putting the area under the $N(E)$ curve equal to 14 states per atom, one concludes that if the width of the band is within a factor of 2 or 3 equal to 0.1 ev, then $(1/N)(d^2N/dE^2)$ is of the right size to account for the quantity $(1/\rho)(d\rho/dT)$ which for α-Pu is equal to -5.4×10^{-2} deg^{-1} and for δ-Pu increases from -1 to -1.5×10^{-4} deg^{-1} as the aluminum content increases from 1 to 10 at. % near 200°K. This width of the band is also in keeping with conclusions arrived at by Lee and Hall.

The particular parabolic shape of the band here assumed leads to a maximum density of states at the Fermi level (for a half-full band) of the order of a hundred states per atom per ev. Somewhat more complicated shapes, as suggested by Friedel and Lee and Hall, Fig. 5(b), could give a lower maximum density of states for a comparably high curvature. The experimental density of states in α- and δ-Pu, as determined from magnetic susceptibility and electronic specific heat data,[11] is 10(±2) states per atom per ev (perhaps as high as 17 states per atom per ev in high-purity plutonium). Depending on band overlap, the number of 5*f* electrons is about five and thus less than half of the band is filled. This gives a positive S as required. The low value of S implies that the Fermi level is just below a maximum in the $N(E)$ curve [Fig. 5(a) or 5(b)].

Lee, Meadon, Hill, and King made[2] the observation that the part of the resistivity of δ-plutonium alloys which is caused by the alloying additions (i.e., apart from the lattice vibrational contribution) is a sum of scattering within the conduction band and of interband scattering. Since the effective Fermi level, according to Eq. (1), decreases with increasing temperature and since the slope dN/dE is positive it follows that the impurity interband scattering will decrease with temperature. It is very difficult to estimate what fraction of the impurity scattering and of the negative temperature coefficient of the resistivity can be accounted for in this way. There is however, an indication that its role is not very big. This is based on the reasonable assumption that this interband scattering would follow an $x(1-x)$ law, where x is the alloy composition. The previously quoted data indicate that $(1/\rho)(d\rho/dT)$ increases by only 50% when x increases from about 0.01 to 0.1. It would appear thus likely that the thermal interband scattering is the predominant factor.

FIG. 5. Possible band shapes.



To sum up, it appears that while the present state of theory and experiment does not permit any detailed conclusions about the band structure, a reasonable band configuration can account for the experimental facts at not too low temperatures.

III. LOW TEMPERATURES

Wilson[21,22] pointed out that under certain conditions the interband scattering is limited by the quantum selection rule

$$\mathbf{k}_1-\mathbf{k}_2=\pm\mathbf{q},$$

where $\mathbf{k}_1$ and $\mathbf{k}_2$ are wave vectors in the two bands and $\mathbf{q}$ is the wave vector of the particular vibrational mode of the lattice which causes the transition. Since at low temperatures only low q vectors, i.e., low lattice frequencies are available many otherwise possible interband transitions will be forbidden.[23] He has shown also that under these conditions the probability of an interband scattering will approach zero as $\exp(-\theta'/T)$, where $k\theta'\ll k\theta_D$ is the energy of the lowest lattice frequency which can produce an interband scattering in a particular band configuration. This applies both to thermally and to impurity excited interband scattering. Wilson's theory is valid under certain conditions of which the two most important ones are that (a) $\theta'\neq0$ or at least is not very small and (b) the description of the wave functions in both bands as Bloch waves is reasonably valid. There is no way to tell *a priori* whether these conditions are satisfied for α and δ plutonium or not. The best check is to verify the exponential dependence and to see whether the resulting values of θ' are reasonable. Figure 6 shows a plot of $\ln(\rho-\rho_0)$, where ρ_0 is the resistivity at absolute zero versus reciprocal temperature for δ-Pu containing seven atomic percent aluminum. Similar plots are obtainable for other compositions of δ-Pu and for α-Pu. It is seen that for temperatures below about 30°K the exponential dependence is very well obeyed. Table I lists the temperatures θ' for various compositions. Since the Debye temperature[11] for α-Pu is about 200°K and for Al-stabilized δ-Pu about[4] 130°K it follows that in all cases θ' is much smaller than θ_D, as required by theory. Once the proximity of $T\sim\theta'$ is reached, lattice frequencies progressively higher than $h\nu'=k\theta'$ become

---

[19] E. C. Ridley, Proc. Roy. Soc. (London) **A247**, 199 (1958).

[20] G. W. Lehman, North American Aviation Report NAA-SR-1839, 1957 (unpublished).

[21] A. H. Wilson, Proc. Roy. Soc. (London) **A167**, 580 (138).

[22] A. H. Wilson, *Theory of Metals* (Cambridge University Press, New York, 1958).

[23] This result holds also if Umklapp processes are included.

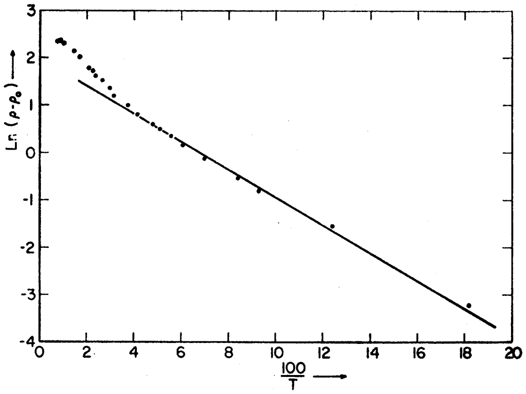


FIG. 6. Resistivity minus residual resistivity (in μohm cm) vs reciprocal absolute temperature for delta plutonium containing 7 at. % aluminum.

rapidly available for causing interband scattering and the resistivity increases faster than exponentially. In the same region of temperature also the normal lattice scattering begins to be significant. At still higher temperatures the interband scattering reaches its full intensity. It appears thus that were it not for the exponential suppression of the interband transitions at low temperature, the residual resistivity would be comparable to $\rho_{\max}$.

It is interesting to note that θ' is roughly equal to one quarter of θ_D both for α- and δ-Pu. In view of the questionable crystallographic uniformity of the 1.2% alloy it is probably safe to assume that θ' is essentially constant within the range of compositions investigated. No information is as yet available about the dependence of θ_D upon Al content in δ-Pu. It would be very interesting to see if there is indeed a close relationship between these two quantities.

Going back to Fig. 2 one can see that ρ_0 is roughly proportional to $x(1-x)$ as one might expect. The irregularities at low x are probably due to partial instability of the undercooled δ phase which results in localized transformation into one of the other phases. Since aluminum is trivalent and the effective valence of cerium in plutonium[24] is about 3.6, there should be not much difference in their direct influence on the electronic configuration. On the other hand, $(1/a)(da/dx)$, where a is the lattice constant,[24,25] is -0.18 for Al and $+0.04$ for Ce. Thus there is appreciably more local lattice distortion and thus a higher ρ_0 in the former case.

The change in the lattice parameter will undoubtedly alter the band width. One would expect cerium to make the bands, especially the $5f$ band, narrower while aluminum would make them wider. Thus, in view of the previous discussion, the coefficient of resistivity would be more negative (and S higher) for cerium than for aluminum alloys. This is just what is observed, the corresponding average values of $d\rho/dT$ being -6.0×10^{-2} and -2.75×10^{-2} μv deg^{-1}. The drop of $\rho_{\max}-\rho_0$ with increasing alloying additions reflects the progressive dilution of plutonium and the perturbation of the band structure. The fact that the drop for cerium is slower than for aluminum is in qualitative accord with the narrowing of the bands in the former case.

TABLE I. Temperature θ' (in °K) for α-Pu and for δ-Pu as function of Al content (in at. %).

α	$\delta(1.2)$	$\delta(2.5)$	$\delta(3.4)$	$\delta(5)$	$\delta(7)$	$\delta(10)$
55	24	32	30	36	29	28

It is interesting to note that aluminum and cerium have a qualitatively similar influence on the resistivity of plutonium in spite of the fact that cerium is a rare earth metal, has an incomplete $4f$ shell, (similar to the incomplete $5f$ shell in plutonium) and a magnetic moment while aluminum is a normal metal and has no magnetic moment. This is another indication that magnetic interactions do not play a significant role in the resistivity anomaly of plutonium. On the other hand,[1] magnetic interactions may be responsible for the fact that at 300°K the resistivity of delta plutonium goes slightly down with increasing Ce content while it goes slightly up with increasing Al (and Lu) content. It should be kept in mind, however, that the total resistivity at 300°K is a sum of several contributions some of which (similarly to ρ_0, Fig. 2) go up, others (similarly to $\rho_{\max}-\rho_0$, Fig. 3) go down with increasing alloy content. It may be that Ce is more effective in lowering the "anomalous" contribution to resistivity than Al (or Lu) at higher temperatures.

The dependence of $T_{\max}$ on alloying content is clearly a combination of the intensity of the interband scattering and of the low-temperature cutoff. Since the latter is controlled by an apparently constant critical frequency $h\nu'=k\theta'$, it follows that the drop of $T_{\max}$ with increasing alloy content as shown in Fig. 4 is only a reflection of the decreasing interband scattering, as illustrated for instance in the drop of $\rho_{\max}-\rho_0$. Again cerium and aluminum behave in a very similar manner, the drop in $T_{\max}$ being more rapid for aluminum, as expected.

Typical values of ρ_0, $\rho_{\max}-\rho_0$, and $T_{\max}$ for α-plutonium of high purity are 25 μohm cm, 144 μohm cm, and 100°K, respectively. As discussed previously its high negative temperature coefficient of resistivity can be accounted for on the band model. A similar argument can be used to make plausible the $\rho_{\max}-\rho_0$ value which is higher than in any δ-Pu alloy. On the other hand, the unusually low $T_{\max}$, which is lower than in most δ-Pu alloys, is a direct result of the much steeper low-temperature cutoff resulting from a high θ' and a high θ_D.

---

[24] K. Gschneidner, *Rare-Earth Alloys* (D. Van Nostrand Company, Princeton, New Jersey, 1961).

[25] F. H. Ellinger, C. C. Land and W. N. Miner, J. Nuclear Materials (to be published).

IV. HIGH TEMPERATURES

The resistivity of some of the stabilized delta phases reaches a minimum somewhere around 300° to 400°C and then increases with temperature. At these temperatures the kT spread at the top of the Fermi distribution is a substantial fraction of the width of the $5f$ band and thus, the usually omitted terms in T^4 have to be included in Eq. (2). It appears that in order to account for the observed behavior the absolute value of d^2N/dE^2 has to increase with increasing E. This can be done by slightly modifying the parabolic $N(E)$ curve proposed above. Any more detailed analysis of the behavior of resistivity at high temperature will require correlation with the thermal expansion coefficient which in many delta alloys is anomalous in this range of temperatures.

It appears thus that, at least qualitatively, the whole resistivity pattern of α and δ plutonium can be made understandable in terms of a band model. There is little doubt, however, that more detailed and especially numerical speculation as to the band shapes in plutonium can be made only with caution.[16,26] The underlying formalism, while rather simple and intuitively attractive, is based on very radical, well-known approximations. There is some hope that the band structure for delta plutonium will be sooner or later calculated in sufficient detail to verify some of the conclusions here reached. There is, unfortunately, very little hope that the same will be possible for the exceedingly complicated alpha phase in which an anomaly in the Hall constant has been recently[27] observed.

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Dr. R. O. Elliott, Dr. K. Gschneidner, Dr. B. Matthias, Dr. C. E. Olsen, Dr. T. A. Sandenaw, and Dr. F. Schonfeld for many stimulating discussions.

---

[26] F. J. Blatt, J. Phys. Chem. Solids **17**, 177 (1961).

[27] R. G. Loasby and J. C. Taylor, Proc. Phys. Soc. (London) **78**, 776 (1961).

PHYSICAL REVIEW VOLUME 125, NUMBER 5 MARCH 1, 1962

"Forbidden" Transitions in the Paramagnetic Resonance of Mn^{++} in Al_2O_3

V. J. Folen
U. S. Naval Research Laboratory, Washington, D. C.

(Received October 27, 1961)

"Forbidden" hyperfine transitions were observed in the electron paramagnetic resonance spectrum of divalent Mn^{55} in Al_2O_3. The intensities and positions of these lines were found to be in good agreement with theory. From measurements of the unequal separations between the $M=\frac{1}{2}\leftrightarrow-\frac{1}{2}$, $\Delta m=\pm1$ transitions in the spectrum, evidence was obtained for a nuclear electric quadrupole interaction in the S-state Mn^{++} ion.

INTRODUCTION

FORBIDDEN hyperfine transitions ($\Delta m\neq0$) have been observed in the electron paramagnetic resonance spectra of Mn^{++} in $ZnSiF_6{:}6H_2O$,[1,2] $(NH_4)_2Zn(SO_4)_2{:}6H_2O$[1], and $CaCO_3$.[3] The intensity of these transitions has been explained[2,4,5] by perturbation expressions involving the combined action of the fine structure D term and the hyperfine A term. On the basis of this theory and recently measured[6] values of the D and A parameters for Mn^{++} in Al_2O_3, "forbidden" transitions should be observable for Mn^{++} in single crystals of this material.

In the present paper, observations of the "forbidden" transitions in the paramagnetic resonance spectrum of Mn^{++} in Al_2O_3 are reported and compared with theory. From measurements of the separations between the $M=\frac{1}{2}\leftrightarrow-\frac{1}{2}$, $\Delta m=\pm1$ transitions in the spectrum, evidence is obtained for the existence of a nuclear electric quadrupole interaction in the S-state Mn^{++} ion.

THEORY

The spin Hamiltonian appropriate for an Mn^{++} ion at a trigonal cation site in Al_2O_3 is given by[7]

$$\begin{aligned}\mathcal{H}=g\beta\mathbf{H}\cdot\mathbf{S}+D[S_z^2-\tfrac{1}{3}S(S+1)]\\+(a/6)[S_\xi^4+S_\eta^4+S_\zeta^4-\tfrac{1}{5}S(S+1)(3S^2+3S-1)]\\+(1/180)F[35S_z^4-30S(S+1)S_z^2+25S_z^2\\-6S(S+1)+3S^2(S+1)^2]+AS_zI_z+B(S_xI_x+S_yI_y)\\-\gamma\beta_N\mathbf{H}\cdot\mathbf{I}+Q'[I_z^2-\tfrac{1}{3}I(I+1)],\end{aligned}\quad(1)$$

where z is the trigonal axis and $\xi\eta\zeta$ refer to the cubic axes.

At an angle θ relative to the z axis, the energy (apart

---

[1] B. Bleaney and D. J. E. Ingram, Proc. Roy. Soc. (London) **A205**, 336 (1951).

[2] E. Friedman and W. Low, Phys. Rev. **120**, 408 (1960).

[3] L. M. Matarrese, J. Chem. Phys. 34, 336 (1961).

[4] G. W. Ludwig and H. H. Woodbury, Bull. Am. Phys. Soc. **5**, 158 (1960).

[5] B. Bleaney and R. S. Rubins, Proc. Phys. Soc. (London) **77**, 103 (1961).

[6] W. Low and J. T. Suss, Phys. Rev. **119**, 132 (1960).

[7] W. Low, *Paramagnetic Resonance in Solids* (Academic Press, Inc., New York, 1960).