Effect of Pressure and Temperature on the Electrical Resistance of Eleven Rare-Earth Metals*

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The electrical resistance of eleven rare-earth metals has been measured as a function of pressure to over 500 kbars at 77 and 296°K. Appropriate isobars between 77 and 296°K have also been obtained. The electronic structure of rare-earth metals is complex with the 4*f* and 5*d* atomic levels relatively close, and both atomic levels split by the crystal field. A wide variety of transitions are observed, many of which must be electronic in character, i.e., they must involve the lowering in energy of one electronic energy band *vis-à-vis* another with increasing pressure and decreasing interatomic distance. These data should provide a partial basis for a theoretical treatment of energy bands in the rare-earth metals.

THE effect of pressure and temperature has been measured on the resistance of eleven rare-earth metals. The metals studied, the source, and the purity of each is summarized in Table I. The high-pressure techniques used have been discussed elsewhere,[1–3] but it is desirable to make a few comments about the measurements. Since there is no certain way to correct for contact resistance, all data are reported as resistances, not resistivities. All isotherms reported were obtained with increasing pressure, since irreversible deformation of Carboloy and pyrophyllite makes pressure measurements impossible with the decreasing pressure. Nevertheless, all features of the curves, discontinuities, maxima, changes in slope, etc., were obtained both on increasing and decreasing pressure. Each isotherm was obtained at least three times, and some with considerable structure were run with as many as twelve different loads. At a number of pressures isobars were obtained. As discussed in other papers[3] these always represent heating from 77 to 296°K. Where the details of the isobar convey particularly interesting information (praseodymium, europium) the entire isobar is presented. In other cases the terminal points are shown on the graphs of the isotherms. Where they do not fall on an isotherm it indicates we were unable to resolve differences in contact resistance at different temperatures. In one or two cases (e.g., praseodymium at 77°K) it was felt desirable to show a "typical isotherm" having all the features shown by each of the isotherms at that temperature, but located relative to the room-temperature isotherm by a series of isobars.

It should be mentioned that in addition to the eleven metals discussed here, data on ytterbium have previously been published in another context.[4]

Bridgman[5,6] measured the resistance of a number of rare earth metals to 65–70 kbars. Our data show all the features (e.g., maximum in resistance of praseodymium at 40 kbars, cusp in cerium at 60 kbars) which he found above about 30 kbars. At lower pressures our results are disguised by changing contact, etc.

It is clear that electrical resistance measurements alone do not provide sufficient information to permit one to unravel the electronic structure of a metal. *A fortiori*, this is true of the rare earths where the 4*f* and 5*d* states are not separated by a very large energy gap.

TABLE I. Source and purity of materials.

Metal	Source	Purity
Ce	Lunex Company	99.96%
Pr	Lunex Company	99.9%
Nd	Lunex Company	99.9%
Sm	Kleber Laboratory	99.9%
Eu	Cerium Metals and Alloys	99.8%
Gd	Cerium Metals and Alloys	Distilled
Tb	Cerium Metals and Alloys	Distilled
Dy	Lunex Company	99.9%
Ho	Kleber Laboratory	99.9%
Er	Kleber Laboratory	99.9%
Tm	Cerium Metals and Alloys	Distilled

* This work was supported in part by the U. S. Atomic Energy Commission.

[1] A. S. Balchan and H. G. Drickamer, Rev. Sci. Instr. **32**, 308 (1961).

[2] H. G. Drickamer and A. S. Balchan in *Modern Very High Pressure Techniques*, edited by R. H. Wentorf, Jr. (Butterworths Scientific Publications Ltd., London, 1962).

[3] R. A. Stager and H. G. Drickamer, Phys. Rev. **131**, 2524 (1963).

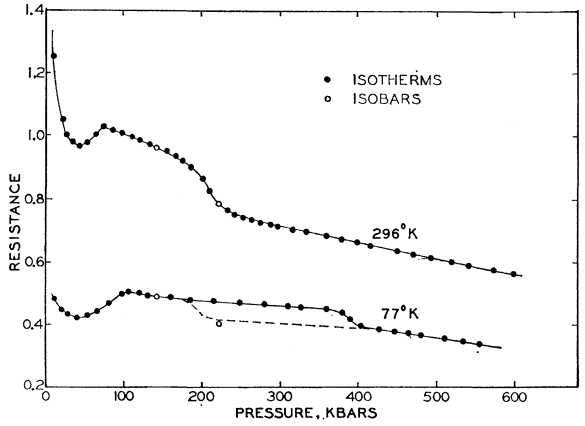

FIG. 1. Resistance versus pressure: cerium.

[4] R. A. Stager and H. G. Drickamer, Science **139**, 1284 (1963).

[5] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **81**, 169 (1952).

[6] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **83**, 1 (1954).

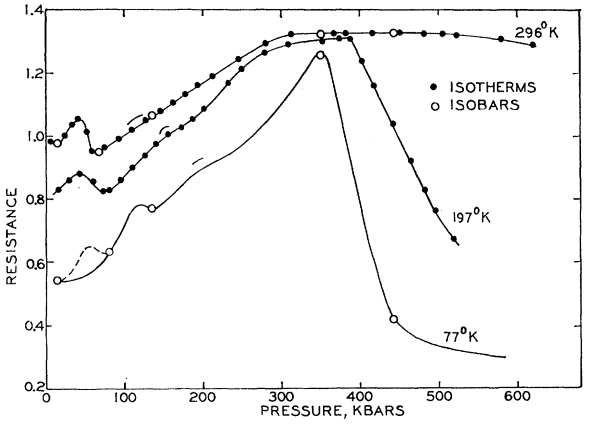

FIG. 2. Resistance versus pressure: praseodymium.

In the crystal lattice, each of these levels are split into two or more bands of varying widths so that there is a multiplicity of possible overlapping states at different pressures. There is also the possibility of changing magnetic state of the system. Ultimately, it is hoped, of course, to make a wide variety of measurements, especially of lattice structure and lattice parameters on these systems, but this is a very long range proposition. Meanwhile, these data should serve as a boundary condition on any theory of electronic structure of these metals, in that any such theory must contain an explanation of our results. It is hoped that they will also encourage theoreticians to attempt such explanations.

In the following paragraphs each of the rare-earth metals studied is discussed individually.

CERIUM

Figure 1 shows two isotherms and terminal points of two isobars. The electronic transition at 5–7 kbars discussed in detail elsewhere[7–9] occurs below our effective range. There is a cusp at 60–65 kbars at 296°K which occurs at 85–95 kbars at 77°K. At about 160 kbars and 296°K, a distinct drop in resistance with some drifting with time occurs. This behavior usually typifies a first order transition. This transition occurs at much higher pressure (~365 kbars) on the 77°K isotherm. However, isobars taken at 220 kbars by cooling from room temperature and reheating indicate that the low-temperature phase at this point is the high-pressure, high-temperature phase, so that the dotted curve probably more nearly represents equilibrium conditions.

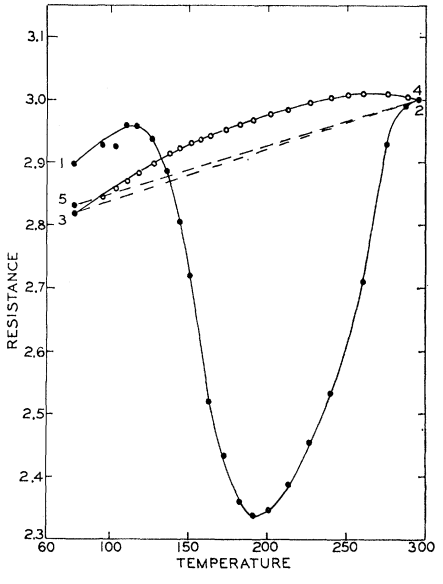

FIG. 3. Resistance versus temperature: praseodymium (350 kbars).

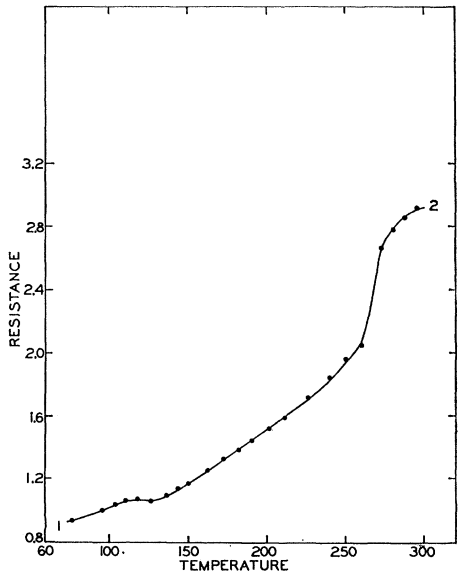

FIG. 4. Resistance versus temperature: praseodymium (440 kbars).

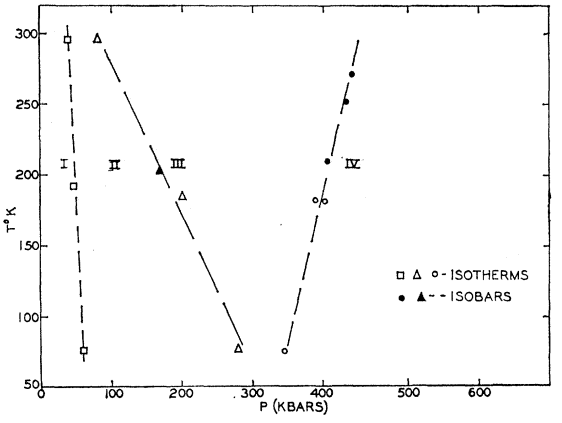

FIG. 5. Tentative phase diagram: praseodymium.

[7] A. W. Lawson and T. Y. Tang, Phys. Rev. **76**, 301 (1949).
[8] A. I. Likhter, N. Riabinin, and L. F. Vereschaguin, Zh. Eksperim. i Teor. Fiz. **33**, 610 (1957) [translation: Soviet Phys.—JETP **6**, 469 (1958)].
[9] R. Herman and C. A. Swenson, J. Chem. Phys. **29**, 398 (1958).

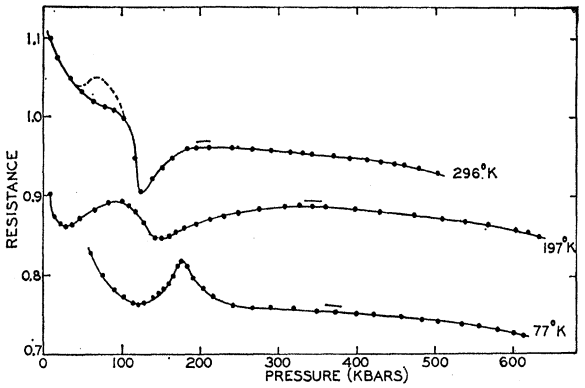

FIG. 6. Resistance versus pressure: neodymium.

PRASEODYMIUM

Figure 2 represents the isotherms for praseodymium. As mentioned earlier, the 77°K isotherm was located by terminal points of a series of isobars. All the features shown are from the twelve 77°K isotherms obtained, but varying contact resistance gave varying placements of the curves so that this represents an average isotherm. The maximum in resistance at 40 kbars and 296°K was also found by Bridgman. At 77°K, it apparently occurs above 100 kbars, but an 80-kbar isotherm indicates that at that point the maximum should already have occurred (dotted curve), so that there is apparently metastability at low temperature. There is a small but definite hump in the curve at

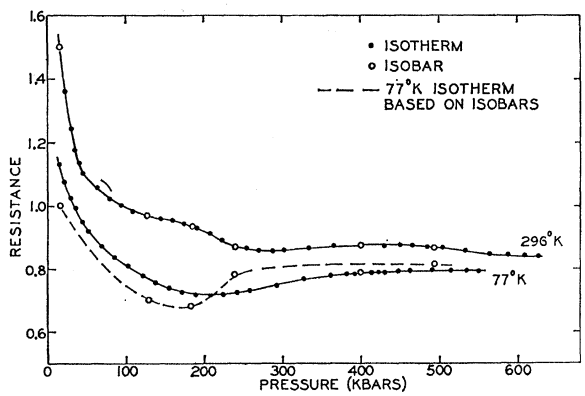

FIG. 7. Resistance versus pressure: samarium.

100 kbars-296°K, 150 kbars-197°K, 190 kbars-77°K, probably representing a change in electronic structure. There is a very broad maximum at 340–360 kbars-296°K. At 197°K the maximum is sharper, and at 77°K it is very sharp. Figure 3 shows a series of isobars at 350 kbars. On the first heating, the material, which is apparently a mixture of phases, goes through a maximum and minimum. Then it stabilizes and successive heatings and coolings reproduce each other with a very small temperature coefficient of resistance. Figure 4 shows an isobar at 440 kbars. The small hump at 130°K was very reproducible. (It was obtained four times.) The sharp rise at 210°K is typical of a first-order phase transition. From a series of such isobars a tentative phase diagram has been developed (Fig. 5).

NEODYMIUM

Three isotherms for neodynium are shown in Fig. 6. At 65 kbars and 296°K, either a point of inflection or a maximum was obtained, depending on the degree that contact had been stabilized. There is a sharp

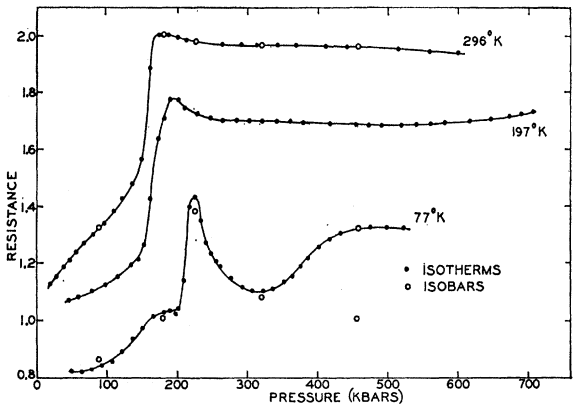

FIG. 8. Resistance versus pressure: europium.

minimum at 120 kbars and a broad maximum beyond 200 kbars. At 197°K, the first maximum is at 100–110 kbars and the minimum at 135–140 kbars. There is a broad maximum above 300 kbars. At 77°K the sharp maximum occurs at 170–175 kbars, the minimum is not observable, and the high pressure maximum occurs as a change of slope above 350 kbars.

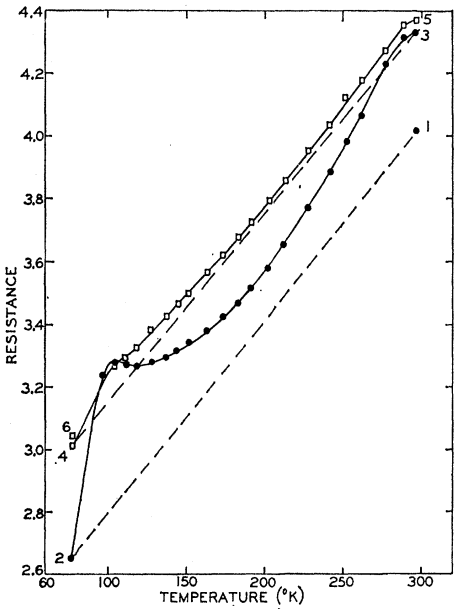

FIG. 9. Resistance versus temperature: europium (85 kbars)

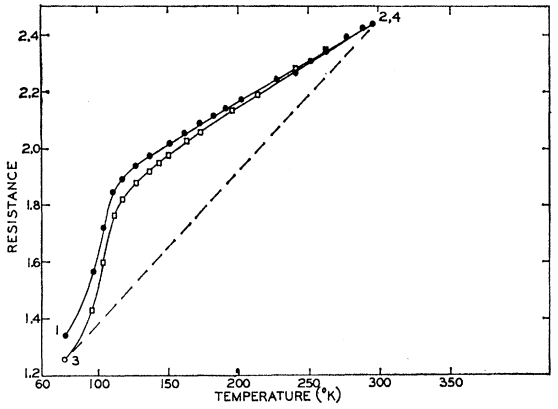

FIG. 10. Resistance versus temperature: europium (310 kbars).

SAMARIUM

Samarium data are shown in Fig. 7. For the 296°K isotherm there is an inflection in the slope at about 50 kbars, a distinct drop in resistance at 160–170 kbars, and a broad maximum near 400 kbars. A 77°K isotherm is shown, as well as a dotted curve constructed from a series of isobars. The most important feature is the distinct rise in resistance above 200 kbars. The very small temperature coefficient of resistance, especially above 300 kbars, is a point worth noting.

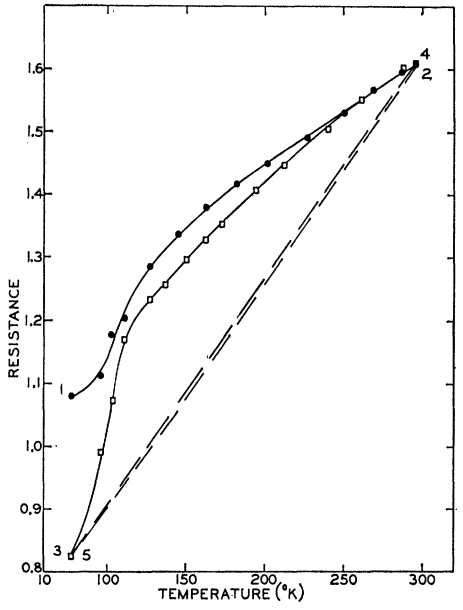

FIG. 11. Resistance versus temperature: europium (460 kbars).

EUROPIUM

The isotherms for europium are shown in Fig. 8. At 296°K the resistance rises with pressure to about 150–160 kbars where there is a very sharp rise typical of a first-order transition. There is a small but distinct maximum at about 175–180 kbars, beyond which the resistance falls very slowly with increasing pressure. The 197°K isotherm is quite similar except that there is a distinct rise in resistance at the highest pressures. The 77°K isotherm has an entirely different appearance, and one which reproduced itself very precisely on nine different loadings. There is a small maximum at 175–180 kbars, a sharp maximum at 210 kbars, a minimum at 310 kbars and a broad maximum near 500 kbars. A very large number of isobars were run. Three of these are shown in Figs. 9–11. Apparently, over most of the pressure range, the phases along an isobar differ at 77 and 296°K. Figure 9 shows an 85-kbar isobar. On heating, one obtains a sharp rise typical of a first order transition, a small maximum which is reproducible but not simply explained, and then the usual metallic rise in resistance with temperature. Recooling evidently does not permit the transition to reverse. Figure 10 shows an isotherm at 310 kbars near the minimum in resistance. There is an initial sharp rise which looks like a transition, and then typically metallic behavior. The curve is entirely reversible and looks exactly in shape like isobars at 210 kbars near the

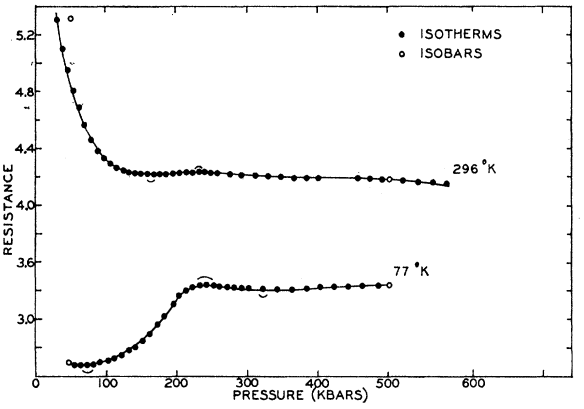

FIG. 12. Resistance versus pressure: terbium.

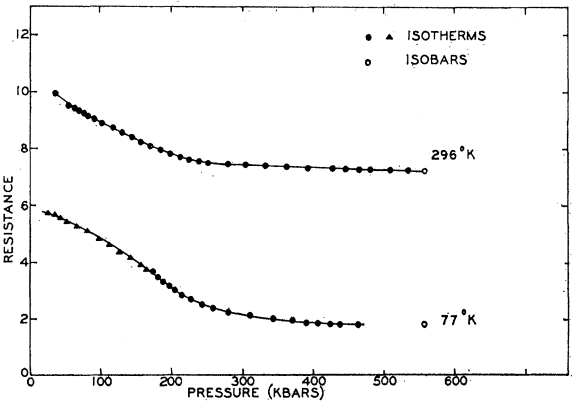

FIG. 13. Resistance versus pressure: gadolinium.

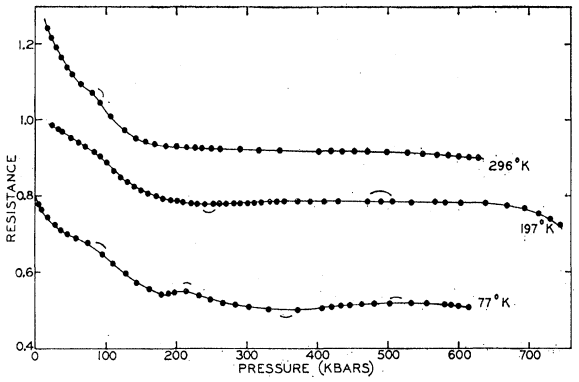

FIG. 14. Resistance versus pressure: dysprosium.

maximum in resistance. A third isobar at 440 kbars is shown in Fig. 11 which is near the last maximum. The material is apparently substantially transformed to the same phase as that at room temperature and high pressure. Upon recooling it apparently undergoes a transition and drops to a low resistance (see terminal point shown in Fig. 9). On reheating, there is initially a transformation and then a smooth rise. These features were reproduced several times.

TERBIUM

Figure 12 shows the terbium isotherms. The 296°K isotherm shows a drop with increasing pressure, a

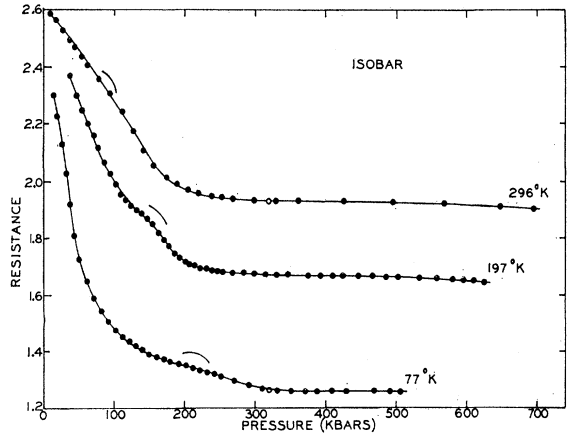

FIG. 15. Resistance versus pressure: holmium.

small but distinct minimum near 150 kbars and a broad maximum near 220–230 kbars. The 77°K isotherm has a minimum at 60–70 kbars, a distinct maximum near 220–230 kbars, and a shallow minimum just above 300 kbars. Although the isotherms differ considerably in shape, no distinct evidence of a first-order transition was found, either from the isotherms or isobars.

GADOLINIUM

Figure 13 shows isotherms for gadolinium. At 296°K there is the possibility of an inflection at low pressure, masked in our apparatus. There is a distinct change in slope above 200 kbars. The 77°K isotherm does not differ radically.

DYSPROSIUM

In Fig. 14 are shown three isotherms for dysprosium. At all three temperatures there is a distinct inflection at 60–80 kbars. The 296°K isotherm has no other prominent features except an increased slope at very high pressure. At 197°K there is a shallow minimum above 200 kbars and a broad maximum below 500 kbars. The

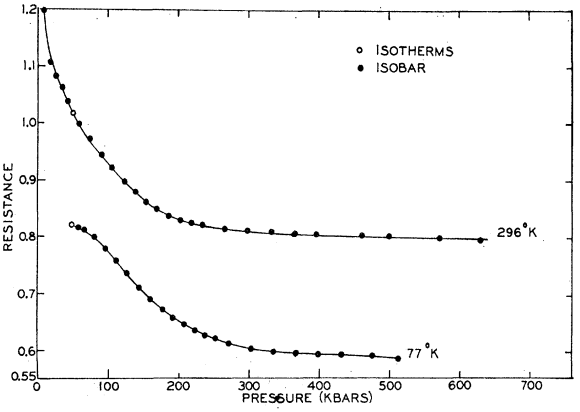

FIG. 16. Resistance versus pressure: erbium.

drop-off at high pressure is very noticeable here. At 77°K there is a distinct maximum at 200–210 kbars, a minimum near 350 kbars and a broad maximum near 500 kbars. These features, which sharpen at low temperature, would seem to be associated with electronic transitions.

HOLMIUM

Isotherms for holmium are shown in Fig. 15. They are similar in general characteristics, with an inflection at 60–80 kbars-296°K which occurs at increasing pressure at lower temperature, but no other important features.

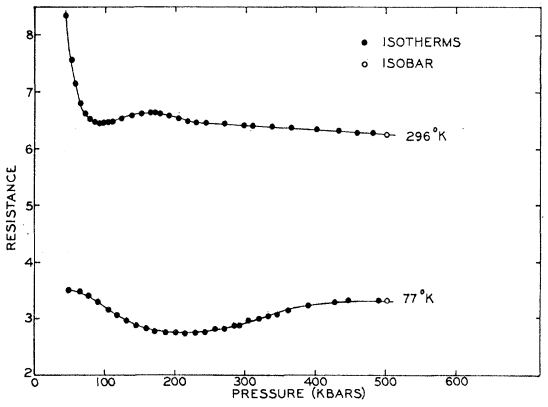

FIG. 17. Resistance versus pressure: thulium.

ERBIUM

The curves for erbium are shown in Fig. 16. The characteristics are much like gadolinium, with the possibility of an inflection at low pressure and no other distinctive features.

THULIUM

The thulium isotherms are shown in Fig. 17. The 296°K isotherm shows a minimum near 60–80 kbars and a maximum at 150–160 kbars. The 77°K isotherm has a minimum at 190–200 kbars.

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Electric Field Effects in Spin Echoes

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A new effect has been observed in electron-spin echo experiments in which an electric field was applied for part of the spin-echo cycle of events. It is found in crystals for which the paramagnetic ion is at a site lacking inversion symmetry, and it is due to the linear shift of the Larmor frequency in the applied electric field. It provides a method for measuring these shifts, and may be used even when the shift is several orders of magnitude smaller than the linewidth. The characteristics of the apparatus used in making these observations are briefly described, and some problems arising in the application of this effect to the measurement of electric field shifts are discussed.

A NUMBER of experiments have been described recently in which an electric field was applied during a spin resonance experiment, and a shift was observed in the resonance frequency.[1–4] First-order shifts proportional to the applied field may be found if the atom or ion responsible for the resonance is in a crystal-field site which lacks inversion symmetry. These shifts are small and are usually only observed at high electric field intensities. In the work reported here an electric field was applied in the form of a voltage step occurring during the cycle of events which characterize an electron-spin echo process. Fields of only a few kV/cm caused major changes in the form of the echo-decay envelope. This effect provides a means of measuring electric-field shifts in paramagnetic resonance with relatively low fields and in broad lines. The magnitude of the shift which can be detected in this way is limited by the width of the individual spin packets which constitute the line, as in the case of the double-resonance (ENDOR) experiments.[5]

The oscilloscope photograph in Fig. 1(a) shows the echo-decay envelope for Ce^{3+} ions in a $CaWO_4$ lattice at 4.2°K and with the Zeeman field along the a axis. The photograph was obtained by superimposing a large number of echo traces corresponding to a series of values of the time τ between the two microwave pulses. The oscilloscope was triggered in each case at the end of the second microwave pulse. Similar photographs have been reproduced elsewhere.[6,7] Figure 1(b) shows the envelope obtained when the experiment is modified by applying an electric field of 450 volts/cm parallel to the c axis immediately after the second microwave pulse and maintaining it until after the echo [see Fig. 3(a)]. In Fig. 1(c) the vertical scale has been magnified to show the null points in the later portions of the envelope more clearly. An electric field applied before the first microwave pulse and maintained until just before the second pulse gave the same result, but no effect at all occurred if the electric field was applied throughout the whole time between the first pulse and the echo.[8]

The role of the electric field in these phenomena may be clarified by giving a summary of the sequence of events in a conventional spin-echo experiment. In any such experiment it is essential that the resonance line should be inhomogeneous, i.e., it should be made up of a large number of spectral components or "spin packets," each with its own independent history of interactions with the applied fields. Ideally a "90° pulse" is followed after an interval τ by a "180° pulse," and during these pulses of microwave power all spin packets are similarly

[1] G. W. Ludwig and H. H. Woodbury, Phys. Rev. Letters **7**, 240 (1961).

[2] J. O. Artman and J. C. Murphy, in *Proceedings of the First International Conference on Paramagnetic Resonance, Jerusalem, 1962* (Academic Press Inc., New York, 1963).

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[4] Electric field effects in nuclear resonance are described by J. Armstrong, N. Bloembergen, and D. Gill, Phys. Rev. Letters **7**, 11 (1961); P. S. Pershan and N. Bloembergen, *ibid.* **7**, 165 (1961).

[5] G. Feher, Phys. Rev. **114**, 1912 (1959).

[6] J. A. Cowen and D. E. Kaplan, Phys. Rev. **124**, 1098 (1961).

[7] W. B. Mims, K. Nassau, and J. D. McGee, Phys. Rev. **123**, 2059 (1961).

[8] In a stimulated echo experiment an electric field applied between microwave pulses one and two, or between microwave pulse three and the echo gave the same effects as in a two-pulse echo experiment. An electric field applied between microwave pulses two and three had no effect.