THE CRYSTAL STRUCTURE OF GADOLINIUM AT 120–370° K

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The crystal structure of polycrystalline gadolinium was studied by x-ray diffraction in the 120–370° K temperature range. The temperature dependences of the lattice constants of the crystal, the atomic volume, and the volume and linear expansion coefficients were obtained. A negative anomaly of the thermal expansion coefficient was observed at 293° K due to a transition of ferromagnetic Gd to the paramagnetic state. With the change of the nature of the temperature dependence of the angle between the direction of the magnetic moment and the [001] axis a maximum was observed in the temperature dependence curve of the atomic volume.

THE study of the crystal structure of the rare-earth metals is of considerable interest in view of the complexity of their magnetic structures and the presence of first and second-order phase transitions. The present work is devoted to a study of the structure of gadolinium, the first of the heavy rare-earth metals series. Gadolinium has the highest ferromagnetic Curie point of all rare-earth metals ($T_C = 293.2°$ K)[1]; its magnetic structure has until recently not been investigated by neutron diffraction because of its large capture cross section for thermal neutrons. The magnetic, electric, and thermal properties of gadolinium at low temperatures have been studied quite adequately.[2-12] Previously it had been assumed that in the temperature range 250–293° K there can exist in gadolinium a helicoidal antiferromagnetic structure which, however, is destroyed even in very weak magnetic fields ($H_c \sim 10$–15 Oe).[2] This assumption is based on analogy with the other rare-earth metals (Tb, Dy, Ho, Er, Tu) in which two magnetic phase transitions occur, paramagnetism-antiferromagnetism, and antiferromagnetism-ferromagnetism, and also on the anomaly of certain physical (including some magnetic) properties at 210–250° K. In the only work devoted to a neutron diffraction investigation of gadolinium at low temperatures[13] it is shown that gadolinium is a normal ferromagnet. In the temperature range 248–293° K the magnetic moment is parallel to the hexagonal ([001]) axis; below this temperature it makes some angle β with it. The value of the angle β reaches a maximum at 195° K (~75°), and then decreases again to 30° at 42° K The results of the neutron diffraction investigation correspond to data on the temperature dependence of the constants of the magnetic anisotropy of gadolinium.[14, 15]

Numerous x-ray investigations of the structure of gadolinium at low temperatures[16-18] have been carried out with low accuracy. To be sure, the anomaly in the temperature dependence of the c parameter near the Curie point (which does not however coincide with T_C obtained from magnetic measurements) has been observed in these investigations, but no detailed study of the temperature dependence of the crystal parameters was made either near T_C or at 210–250° K. The purpose of this work has been a precise study of the crystal structure in the temperature range 120–370°K by means of x-ray structure analysis.

The investigated material was 99.7 per cent pure polycrystalline gadolinium. The 9 × 13 × 1.5 mm samples were cut by electro-erosion, ground, and polished. In order to remove internal stresses, the following heat treatment was used: a fifteen-minute annealing in vacuum at 1050° C and slow cooling of the samples to room temperature. Such a heat treatment of gadolinium did not lead to noticeable growth of the grains: a small-grain structure with a mean crystallite size of about 10 microns was observed metallographically.

The study of the crystal structure was carried out on an URS-501 x-ray diffractometer, equipped with a low-temperature attachment, using a previously described method.[19] To measure the parameters of the hexagonal crystal lattice of gadolinium, the peaks due to the (203) planes (diffraction angle θ at room temperature ~70°) and (104) planes ($\theta \sim 65°45'$) were recorded with

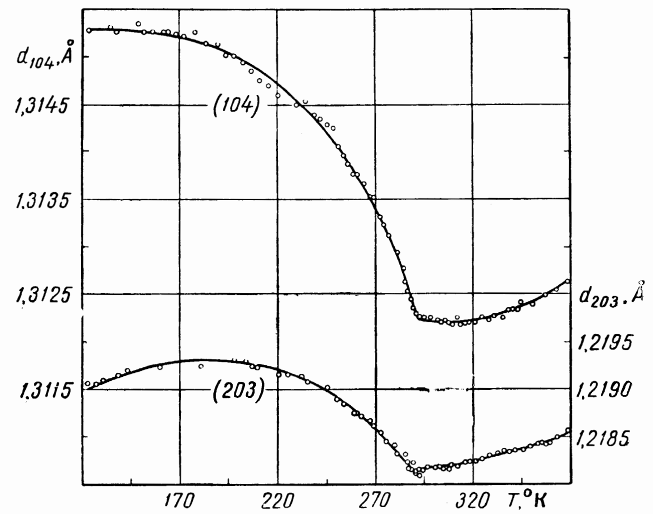

FIG. 1. Temperature dependence of the interplanar distances of the (104) and (203) planes.

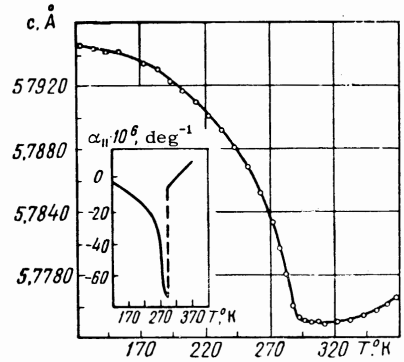

FIG. 3. Temperature dependence of the parameter c and of the linear expansion coefficient $\alpha_{\|}$.

chromium radiation. The (104) and (203) lines were sufficiently intense on the patterns of the polycrystalline metal; the $K\alpha_1$–$K\alpha_2$ doublets were satisfactorily resolved.

Figure 1 shows the temperature dependences of d_{203} and d_{104}. On the $d_{104}(T)$ curve a strong decrease of the interplanar spacing is observed on increasing the temperature to T_C; at $T > T_C$, d_{104} increases with temperature. The interplanar spacing d_{203} depends weakly on the temperature; a small maximum is observed on the $d_{203}(T)$ curve at ~ 200°K, and in the paramagnetic region the interplanar spacing increases with temperature. It can thus be seen from Fig. 1 that the thermal expansion of gadolinium is anomalous.

The temperature dependences of the lattice parameters of gadolinium (Figs. 2 and 3) were calculated from the $d_{104}(T)$ and $d_{203}(T)$ curves. The values of the true linear expansion coefficients $\alpha_{\perp} = a^{-1}\,da/dT$ and $\alpha_{\|} = c^{-1}\,dc/dT$ (the inserts of Figs. 2 and 3) were obtained by graphical integration of the curves a(T) and c(T). The temperature

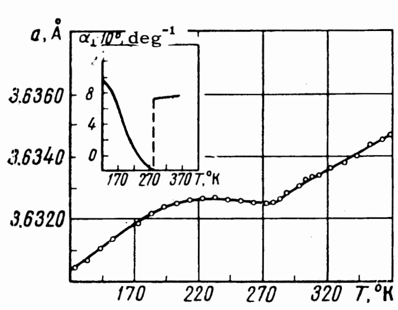

FIG. 2. Temperature dependence of the parameter a and of the linear expansion coefficient $\alpha_{\perp}$.

dependences of the lattice constants and of the thermal expansion of gadolinium are rather complex: c decreases with increasing temperature up to T_C and then increases; a increases with increasing temperature but very weakly, and a small maximum is observed at about 220° K; in the paramagnetic region a hardly increases with increasing temperature. Near the temperature of the ferromagnetic transition the $\alpha_{\perp}(T)$ and $\alpha_{\|}(T)$ curves exhibit λ-point type anomalies whose "sign" is negative. A negative λ-point anomaly of the linear expansion coefficient along the [001] axis was noted in [7, 12], but according to the results of these papers the λ anomaly on the $\alpha_{\perp}(T)$ curve is positive, although the quantity $\Delta\alpha_{\perp}$ is, as is well known, at the limit of the accuracy of the measurements. The contradiction between our data and the results of the dilatometric measurements[7, 12] may be related both to the inappreciable change of the parameter a near T_C (see Fig. 2), which makes it difficult to determine the linear expansion coefficient reliably, and also to the possible difference in the purity of the investigated metal. We note also that in determining T_C from the minimum on the $\alpha_{\perp}(T)$ and $\alpha_{\|}(T)$ curves a rather large anisotropy of the ferromagnetic Curie point is observed (~ 10° K) which exceeds the possible measurement errors. The anisotropy of the Curie temperature was indicated in the work of K. P. Belov and his co-workers,[2] however from results of magnetic measurements $\Delta T_C = 1.5$° K.

In view of the fact that the linear thermal expansion characteristics of gadolinium (a, c, $\alpha_{\perp}$, $\alpha_{\|}$) exhibit very strong anisotropy, it is convenient to consider the temperature dependence of quantities characterizing the volume expansion: the volume per atom ($V_{at} = a^2c\sqrt{3}/4$) and the volume expansion coefficient ($\alpha_V = V_{at}^{-1}dV_{at}/dT = 2\alpha_{\perp} + \alpha_{\|}$). The corresponding graphs are presented in Fig. 4. On the $V_{at}(T)$ curve a maximum is observed at

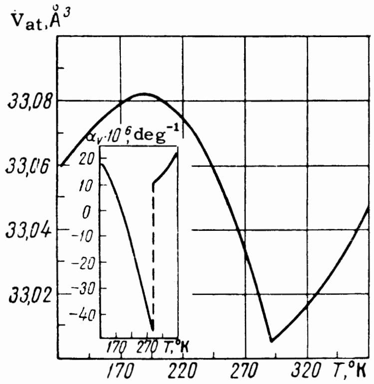

FIG. 4. Temperature dependence of the atomic volume and of the volume expansion coefficient.

~ 200° K and a sharp minimum at the Curie point (293° K), whereas on the $\alpha_V(T)$ curve no special features are observed at 200° K (the decreasing α_V passes at this point through zero), and a clearly pronounced negative λ anomaly occurs at 293° K.

Studies of the crystal structure of gadolinium indicate that it is strongly dependent on the changes in the magnetic structure. At the Curie point the negative character of the λ anomaly of the thermal expansion coefficients (α_V, $\alpha_\perp$, and $\alpha_\parallel$) is, in accordance with L. D. Landau's theory of second-order phase transitions, in agreement with the experimentally obtained[21] negative value of the derivative $dT_C/dp = -1.2 \times 10^{-3}$ deg/atm. The temperature of the λ anomaly of the volume expansion coefficient (293° K) coincides within the limits of the accuracy of the measurements with the most recent values of T_C from the results of magnetic measurements.[1)][1, 11] The complex nature of the dependence of $V_{at}(T)$ in the ferromagnetic region is related to the complex nature of the temperature dependence of the angle β between the direction of the magnetic moment and the hexagonal axis. At temperatures below ~200° K when $d\beta/dt > 0$ the thermal expansion is positive ($\alpha_V > 0$); at temperatures above ~ 200° K when $d\beta/dt < 0$ the thermal expansion is negative. The temperature "drift" of the angle β leads to very complex dependences a(T), c(T), $d_{203}(T)$, and $d_{104}(T)$ for $T < T_C$. The fact that at ~200° K, when the derivative $d\beta/dT$ changes sign and a maximum is observed on the curve of the temperature dependence of the atomic volume, there is no anomaly on the $\alpha_V(T)$ curve means that no phase transition occurs at this temperature.

A macroscopic result of the change in the direction of the magnetic moment relative to the [001] axis is the extremal character of the temperature dependence of the magnetization (σ). Experimentally the maximum on the $\sigma(T)$ curve at 200° K was observed in the work of Belov and his co-workers.[2] Inasmuch as to a first approximation the "anomalous" part of the thermal expansion (i.e., the thermal expansion V(T) with the value of V obtained by extrapolation from the paramagnetic region subtracted) is proportional to σ^2,[22] a maximum should be observed on the V(T) curve (Fig. 4).

[1)]The nature of the anisotropy of T_C along the a and c axes is so far not altogether clear.

[1] W. C. Koehler, J. Appl. Phys. **36**, 1078 (1965).

[2] K. P. Belov, R. Z. Levitin, and S. A. Nikitin, UFN **82**, 449 (1964), Soviet Phys. Uspekhi **7**, 179 (1964); K. P. Belov, R. Z. Levitin, S. A. Nikitin, and A. V. Ped'ko, JETP **40**, 1562 (1961), Soviet Phys. JETP **13**, 1096 (1961); K. P. Belov and A. V. Ped'ko, JETP **42**, 87 (1962), Soviet Phys. JETP **15**, 62 (1962); K. P. Belov, Yu. V. Ergin, R. Z. Levitin, and A. V. Ped'ko, JETP **47**, 2080 (1964), Soviet Phys. JETP **20**, 1397 (1965); K. P. Belov and R. Z. Levitin, Sb. Voprosy teorii i primeneniya RZM (Coll. Problems in the Theory and Application of Rare-earth Metals), Nauka, 1964, p. 42.

[3] H. E. Nigh, S. Legvold, and F. H. Spedding, Phys. Rev. **132**, 1092 (1963).

[4] A. S. Marotto and K. J. Tauer, J. Phys. Soc. Japan **18**, 310 (1963).

[5] N. V. Volkenshteĭn, G. V. Fedorov, E. V. Galoshina, and V. E. Startsev, Sb. Voprosy teorii i primeneniya RZM (Coll. Problems in the Theory and Application of Rare-earth Metals), Nauka, 1964, p. 79.

[6] S. Legvold, F. H. Spedding, F. Barson, and J. Elliot, Rev. Modern Phys. **25**, 129 (1953); Phys. Rev. **91**, 28 (1953).

[7] R. M. Bozorth and J. Wakiyama, J. Phys. Soc. Japan **17**, 1669, 1970 (1962); **18**, 97 (1963); J. Appl. Phys. **34**, 1351 (1963).

[8] W. E. Colman and A. S. Pavlovic, J. Phys. Chem. Solids **26**, 690 (1965).

[9] M. Trombe and M. Foex, Compt. rend. **235**, 42 (1952).

[10] K. R. Birss, Proc. Roy. Soc. **255A**, 398 (1960).

[11] G. D. Graham, J. Appl. Phys. **36**, 1135 (1965).

[12] Yu. V. Ergin, JETP **48**, 1062 (1965), Soviet Phys. JETP **21**, 709 (1965).

[13] G. Will, R. Nathans, and H. A. Alperin, J. Appl. Phys. **35**, 1045 (1964).

[14] W. D. Corner, W. C. Roe, and K. N. R. Taylor, Proc. Phys. Soc. **80**, 927 (1962).

[15] G. D. Graham, J. Appl. Phys. **34**, 1341 (1963).
[16] J. R. Banister, S. Legvold, and F. H. Spedding, Phys. Rev. **94**, 1140 (1954).
[17] F. J. Darnell, Phys. Rev. **130**, 1825 (1963).
[18] F. J. Darnell and W. H. Cloud, J. Appl. Phys. **35**, 935 (1964).
[19] Yu. N. Smirnov and V. A. Finkel', JETP **47**, 476 (1964), Soviet Phys. JETP **20**, 315 (1965).
[20] L. D. Landau and E. M. Lifshitz, Statistical Physics, Addison-Wesley, 1958.
[21] L. Patrick, Phys. Rev. **93**, 384 (1954); S. H. Liu, Phys. Rev. **127**, 1889 (1962).
[22] P. Chevenard, Compt. rend. **172**, 1655 (1921); K. P. Belov and N. K. Panina, DAN SSSR **111**, 985 (1956), Soviet Phys. Doklady **1**, 732 (1957).

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