Loss Mechanisms in Spinel Ferrites

J. K. GALT AND E. G. SPENCER
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received April 17, 1962)

New data on ferrimagnetic resonance linewidth at 9200 Mc/sec in a ferrite of composition $(NiO)_{0.75}$-$(FeO)_{0.25}Fe_2O_3$ are presented. These data are compared with earlier observations of ferrimagnetic resonance linewidth at 24 000 Mc/sec on the same material in order to distinguish between two theoretical analyses of the mechanism of loss involved.

I. INTRODUCTION

LOSS mechanisms in nonmetallic ferromagnetic materials have been a subject of interest for some years past. Two such mechanisms which have been studied in some detail concern us in this paper. One of these,[1–3] which has been discussed primarily in connection with ferrites having the spinel structure, is the valence electron exchange which occurs between Fe^{++} and Fe^{3+} ions when Fe^{++} ions are present. The other mechanism, which has been discussed primarily in connection with materials having the garnet structure,[4] is the damping effect of magnetic impurity ions whose magnetic moments are coupled both to the crystal lattice and to the magnetic lattice.

These two mechanisms have given rise to two different theoretical analyses. White[5] has suggested, however, that, in fact, the losses associated with Fe^{++} ions in the spinel ferrites are, for the most part, described best in terms of the mechanism and the theoretical analysis developed to account for losses due to the presence of magnetic impurities in the garnets. The purpose of the present paper is to present some ferrimagnetic resonance linewidth data on nickel-iron spinel ferrites which are relevant to this question, and to discuss the fit between these and the older data, on the one hand, and the two theoretical analyses, on the other, with a view to discriminating between the two theories as applied to this case. The new data are an extension of the results of earlier experiments on nickel-iron ferrite single crystals participated in by one of us,[1] and were, in fact, obtained on the same single-crystal sphere.

II. THEORY

The theory originally developed to account for the losses associated with divalent iron in ferrites will be referred to as the slow relaxation theory. It was worked out from two points of view,[1,3] and it is based on the idea that the equilibrium arrangement of the Fe^{++} and Fe^{3+} ions depends on the direction of the magnetization in the crystal lattice. The model used in these theories assumed, first, that the coupling between the Fe^{3+} and Fe^{++} ions was large compared to the coupling of the Fe^{++} ions to the crystal, and second, that if τ is the relaxation time for the rearrangement of the ions, the experimental frequency ω is comparable at the relevant temperatures to the relaxation frequency $1/\tau$. In the notation of reference 4, the two sublattices which include all except the Fe^{++} ions are assumed to be tightly coupled and characterized as lattice A, while the Fe^{++} ions constitute lattice B. The coupling between Fe^{3+} and Fe^{++} ions may be characterized by a frequency ω_{AB}, and the coupling between the Fe^{++} ions and the lattice is characterized by $1/\tau$. The slow-relaxation theory assumes that

$$\omega_{AB}\gg 1/\tau,\qquad \omega=O(1/\tau). \tag{1}$$

A theory of losses based on a generalization of this model was first worked out by Néel.[6] The simpler and less detailed of the two slow-relaxation theories gives a thermodynamical analysis of this mechanism in terms of the relaxation of torques on the magnetization derived from part of the free energy. It gives for the ferrimagnetic resonance linewidth (see reference 1):

$$2\Delta H=\frac{1}{M_z}\left[\left(\frac{\partial^2 g_{1\infty}}{\partial\theta_x^2}\right)_{\theta_x=0}+\left(\frac{\partial^2 g_{1\infty}}{\partial\theta_y^2}\right)_{\theta_y=0}\right]\frac{\omega\tau}{1+\omega^2\tau^2}, \tag{2}$$

where $2\Delta H$ is the full linewidth at half-power points, τ is the torque relaxation time, and M_z is the component of the magnetization along the applied magnetic field. Also, $g_{1\infty}$ is a term in the free energy of the form:

$$g_{1\infty}=a(\theta_x^2+\theta_y^2)+K_{1r}(\alpha_1^2\alpha_2^2+\alpha_2^2\alpha_3^2+\alpha_3^2\alpha_1^2), \tag{3}$$

where α_1, α_2, α_3 are the direction cosines of the magnetization with respect to the crystal axes, and θ_x and θ_y are angles which measure small deviations of the magnetization from the z axis along which the steady magnetic field is applied. The constants a and K_{1r} determine the magnitude of the effect. When both terms in Eq. (3) are expressed in terms of θ_x and θ_y,

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it may be substituted in Eq. (3). This leads, at the temperature for which $\omega\tau=1$, to a peak in the linewidth as a function of temperature for measurements made at a given frequency. The magnitude of this peak is anisotropic with cubic symmetry. For measurements made at two different frequencies, this linewidth peak occurs at two different temperatures since τ is temperature dependent according to the relation

$$\tau=\tau_{\infty}e^{\epsilon/kT}, \tag{4}$$

where ϵ is the activation energy for the ion rearrangement. From Eq. (4) and measurements of the change in the temperature at which this peak occurs as frequency changes, ϵ may be determined from the fact that $\omega\tau$ is unity at the linewidth peak. The magnitude of the linewidth peak is, however, independent of frequency on this slow relaxation theory.

The second theory we wish to consider, which was developed originally by Kittel to account for ferrimagnetic resonance linewidths as observed in certain garnets,[4] is referred to here and elsewhere as the fast relaxation theory. In the notation introduced above, it is based first on the idea that the moments of certain ions—Fe^{++} ions in the present case—are so tightly coupled to the crystal lattice that the relaxation frequency $1/\tau'$ is much larger than the experimental frequency ω at all relevant temperatures. Secondly, it is based on the assumption that at relevant temperatures $1/\tau'$ is comparable with the coupling frequency ω_{AB} between the two types of ions—Fe^{3+} and Fe^{++} in our case. In short, this theory assumes that

$$\begin{aligned}\omega_{AB}&=O(1/\tau'),\\ \omega&\ll 1/\tau'.\end{aligned} \tag{5}$$

It leads to the following expressions for the ferrimagnetic resonance linewidth (see reference 4):

$$2\Delta H=(N_B/N_A)(\omega_{AB}2\tau/\gamma)(\omega/kT);\quad \omega_{AB}\tau'\ll 1, \tag{6}$$

$$2\Delta H=(M_B/M_A)(\gamma/\omega_{AB}\tau);\quad \omega_{AB}\tau'\gg 1, \tag{7}$$

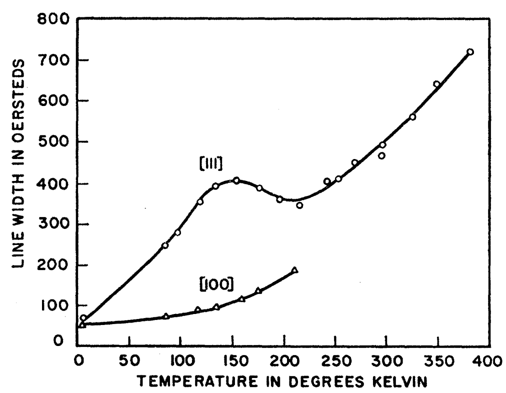

FIG. 1. Ferromagnetic resonance linewidth at 24 000 Mc/sec vs temperature in a sphere of $(NiO)_{0.75}(FeO)_{0.25}Fe_2O_3$ which is 0.009 in. in diameter. The crystal directions associated with each curve give the orientation of B_{dc}. (After reference 1.)

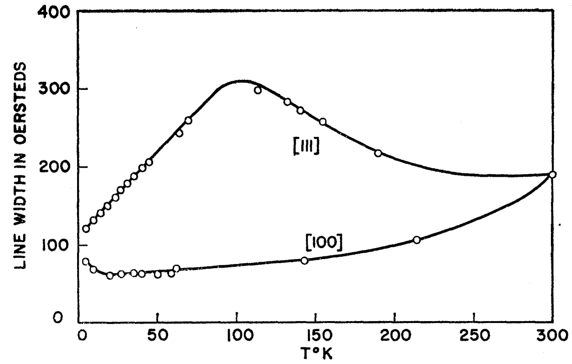

FIG. 2. Ferromagnetic resonance linewidth of 9200 Mc/sec vs temperature for the same 0.009-in.-diameter sphere of $(NiO)_{0.75}(FeO)_{0.25}Fe_2O_3$ on which the results shown in Fig. 1 were obtained. The crystal directions associated with each curve give the orientation of B_{dc}.

where N_B is the number of ions on lattice B (Fe^{++} in the present case), N_A is the number of ions on lattice A, M_B is the magnetization of the B lattice, M_A is the magnetization of the A lattice, ω is the experimental frequency, γ the gyromagnetic ratio, τ' the relaxation time for the fast relaxing ions, and ω_{AB} the frequency which measures the coupling between the fast relaxing ions and the rest of the magnetic lattice. These relationships also lead to a peak in the linewidth as a function of temperature for measurements made at a given frequency, but the peak does not change in temperature as the measuring frequency changes. The peak occurs when $\omega_{AB}\tau'$ is unity. Furthermore, this fast relaxation theory predicts that in contradistinction to the slow relaxation theory the amplitude of the peak is proportional to the experimental frequency. The anisotropy in the linewidth peak to be expected on the basis of the fast relaxation theory also shows the cubic symmetry of the crystal.

III. EXPERIMENTAL RESULTS

As mentioned earlier, ferrimagnetic resonance linewidth has been studied previously in nickel-iron ferrite single crystals at 24 000 Mc/sec. Reference 1 gives the experimental results of this study in some detail. We shall be concerned here with the composition $(NiO)_{0.75}(FeO)_{0.25}Fe_2O_3$. In Fig. 1 is shown a plot of data abstracted from this reference which gives the variation as a function of temperature of the linewidths measured with steady field along ⟨111⟩ and ⟨100⟩ directions. The data shown here are based on those given in reference 1 for the sphere 0.009 in. in diameter, on which the most complete set of results was obtained.

In Fig. 2 are shown new results obtained by us at 9200 Mc/sec on the same sphere of ferrite used to obtain the data in Fig. 1. Here again are plotted versus temperature the ferrimagnetic resonance linewidths measured with steady field along ⟨111⟩ and ⟨100⟩ axes.

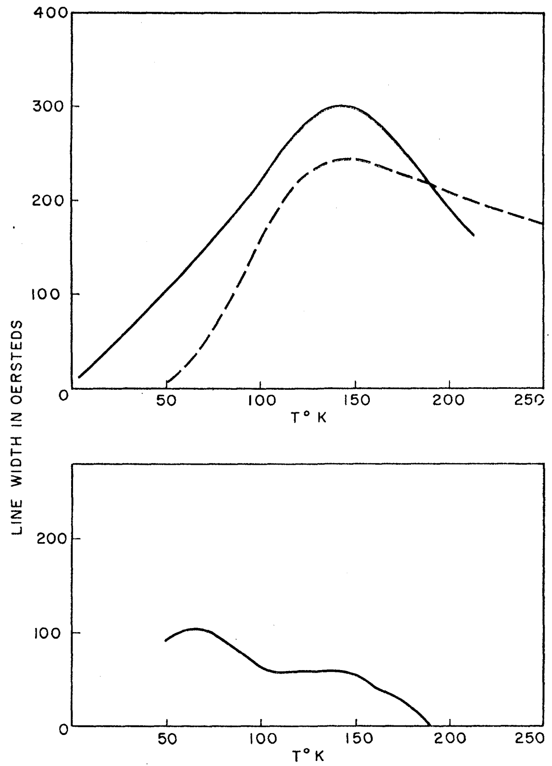

FIG. 3. Top: The solid line is the difference between ferromagnetic resonance linewidth observed with B_{dc} along $\langle 111\rangle$ and that observed with B_{dc} along $\langle 100\rangle$ at 24000 Mc/sec in 0.009-in.-diam sphere of $(NiO)_{0.75}(FeO)_{0.25}Fe_2O_3$. The dashed line is the best fit of the slow relaxation theory to the solid line consistent with 9200-Mc/sec data. (See Fig. 4.) Bottom: The difference between the solid and the dashed lines shown in plot at top.

IV. ANALYSIS

Certain qualitative conclusions emerge from inspection of the data presented in Figs. 1 and 2. The most important of these for our present purposes are that the peak changes in temperature as the measuring frequency changes, while the amplitude of the peak varies relatively little with the measuring frequency. These two conclusions suggest to us that the experimental frequency ω is comparable to the relaxation frequency, and, therefore, that the slow relaxation theory fits the data better than the fast relaxation theory. The observed variation of about 25% in the linewidth peak does suggest, however, that the slow relaxation theory is not completely valid and that deviations from it play a significant, although minor, role.

Having drawn the qualitative conclusion that the slow relaxation theory is the more relevant one, we now fit the results of both frequencies as well as possible to Eq. (2) with a view to exploring the matter more quantitatively.

The top of Fig. 3 shows, as a solid line, a plot of the *difference* in the values of the linewidth as observed at 24000 Mc/sec with the magnetic field along the two directions for which it is plotted in Fig. 1. The top of Fig. 4 shows, as a solid line, the same difference as obtained from the observations at 9300 Mc/sec shown in Fig. 2. These curves represent the linewidth when the steady magnetic field is along the $\langle 111\rangle$ direction neglecting contributions which are isotropic, which we shall do in this work. There are two such contributions in this case, one which is temperature independent and whose origin is not clear, and another from eddy-current effects which is especially important at 24 000 Mc/sec. It is this latter contribution which causes the curves at 24 000 Mc/sec to turn up at the higher temperatures. These corrections and the precision of the original measurements are such that we estimate the accuracy of the peak height in both cases to be about $\pm 10\%$. It may be noted that earlier work (reference 1) used a peak height of 320 Oe rather than the 300 shown here in Fig. 3, while Clogston[3] used 308 for the same number. These larger numbers reflect in part data taken on other, smaller, spheres. The contribution of eddy currents at the higher temperatures makes the 24 000 Mc/sec curve less precise there than $\pm 10\%$.

In order to fit the solid lines in Figs. 3 and 4 to Eq. (2) note first from Figs. 1 and 2 that the linewidth peak where $\omega\tau = 1$, occurs at $\tau = 145°$K when $\omega/2\pi = 24\,000$ Mc/sec and at $\tau = 100°$K when $\omega/2\pi = 9200$ Mc/sec. These facts and Eq. (4) lead to the follow-

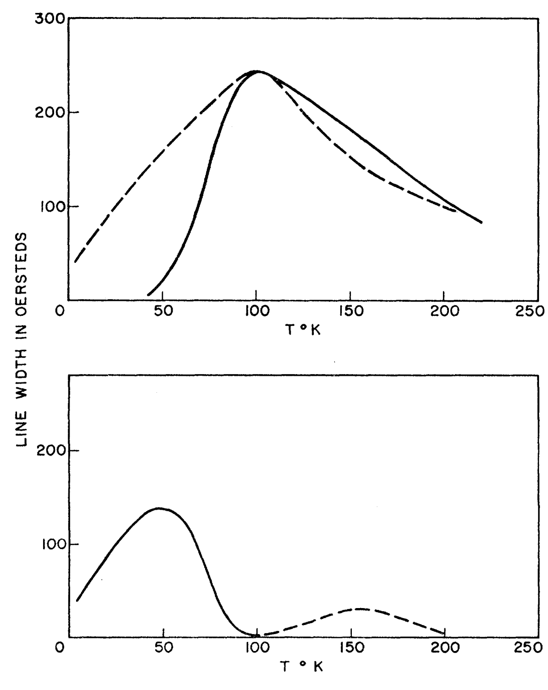

FIG. 4. Top: The solid line is the difference between ferromagnetic resonance linewidth observed with B_{dc} along $\langle 111\rangle$ and that observed with B_{dc} along $\langle 100\rangle$ at 9200 Mc/sec in same 0.009-in.-diam sphere of $(NiO)_{0.75}(FeO)_{0.25}Fe_2O_3$ as data in Fig. 3. The dashed line is the best fit of slow relaxation theory to solid line. Bottom: The difference between the solid and the dashed lines shown in plot at top.

ing values for ϵ and τ_∞:

$$\begin{aligned}\epsilon&=0.027\text{ eV},\\ \tau_\infty&=7.5\times10^{-13}\text{ sec.}\end{aligned}\tag{8}$$

These values are also slightly different from those in reference 1, partly because the numbers used there were from data taken on a smaller sphere; however, the differences are not significant here, and the present method is a more satisfactory way to determine these parameters than that used in reference 1. Next, if $g_{1\infty}$ as given by Eq. (3) is differentiated and used in Eq. (2), the result is

$$2\Delta H=\frac{1}{M_z}[4(a+K_{1r})-20K_{1r}(\tfrac{1}{4}\sin^4\theta_0+\sin^2\theta_0\cos^2\theta_0)]\frac{\omega\tau}{1+(\omega\tau)^2},\tag{9}$$

where θ_0 is the angle between the magnetization and the $\langle100\rangle$ direction in the (110) plane. First this is fitted at $\omega\tau=1$. The fact that the relevant linewidth contribution is zero when the magnetic field and, therefore, the magnetization is along $\langle100\rangle$ (for which $\theta_0=0$) leads to the result $a=-K_{1r}$. The magnitude of these quantities is then determined from the peak value of $2\Delta H$ when the magnetization is along the $\langle111\rangle$ direction. Since the slow relaxation theory predicts this quantity to be independent of frequency and the results in Figs. 3 and 4 show some variation, the value to be used here is indeterminate between the 300 Oe obtained at 24 000 Mc/sec and the 230 Oe obtained at 9200 Mc/sec. We have used the value obtained at 9200 Mc/sec, because the lack of eddy-current effects at this frequency suggest that data obtained there are better. This gives

$$\alpha=-K_{1r}=2.5\times10^4\text{ ergs/cc.}\tag{10}$$

With these parameters, and $\theta_0=\sin^{-1}(\sqrt{2}/\sqrt{3})$, Eq. (9) gives the dashed lines in Figs. 3 and 4.

It seems clear from Figs. 3 and 4 that while a relatively small amount of frequency dependence in the amplitude of the linewidth peak is apparent, the most important deviation of experiment from the theoretical result is at low temperatures where this frequency dependence is not important. If the theoretical curves shown dashed in the top halves of Figs. 3 and 4 are subtracted from the experimental curves, a remainder is obtained which is plotted in the bottom halves of Figs. 3 and 4. In the low temperature region, these remainder curves are linewidth peaks themselves, and indicate the presence of at least two linewidth maxima at each frequency. The high-temperature end of these curves is relatively small percentagewise, and is just enough larger than experimental error to indicate some frequency dependence in the linewidth peak. These curves are reproduced in Fig. 5, and they show that

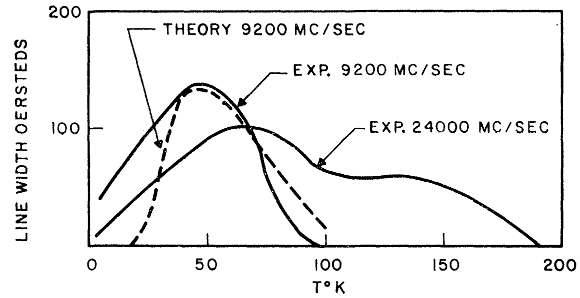

FIG. 5. Solid lines: difference between experimental data as given in Figs. 3 and 4 by solid lines and best slow relaxation theory fit, also as given in Figs. 3 and 4. Dashed line: best fit of slow relaxation theory to curve given by solid line for 9200 Mc/sec.

the second linewidth maximum behaves very similarly to the first; that is, its position depends on the frequency of the measurement, whereas its amplitude does not depend on it very much. In fact, the height of the peak at 24 000 Mc/sec appears slightly larger than that obtained from the 9200-Mc/sec data, but we do not regard this difference as significant, especially since no experimental observations were actually made at 24 000 Mc/sec between 85 and 4°K, and the curve in that region is only extrapolated. The important point is that this peak follows the frequency dependence associated with the slow-relaxation theory.

Since the peaks shown by solid lines in Fig. 5 are obtained by subtraction, a fit to Eq. (2) must be interpreted with some care, especially for the 24 000-Mc/sec data. The 9200-Mc/sec data, however, seem to us sufficiently precise to justify this, and the dashed line in Fig. 5 shows the result. There is some uncertainty in the determination of the activation energy because of the uncertainties which arise from subtraction, but we find the following parameters in the process of working out the dashed line in Fig. 5:

$$\begin{aligned}\epsilon&=0.020\pm0.005\text{ eV},\\ \tau_\infty&=0.34-4.04\times10^{-13}\text{ sec},\\ \alpha&=-K_{1r}=1.4\times10^4\text{ ergs/cc.}\end{aligned}\tag{11}$$

It may be noted that the presence of this second peak, together with the first, accounts for more of the variation of K_1 with temperature than was done in reference 1. The presence of this second linewidth peak may also be used in the analysis of reference 3 to improve agreement between theory and experiment.

The deviation apparent in Fig. 5 between the solid line derived from the 9200-Mc/sec data and the dashed line derived from theory indicates that if the experimental results are to be fitted precisely at the lowest temperatures, the analysis must be complicated still further. It seems to us unwise to do so on the basis of the simple theory presented here, and we have, therefore, not investigated these very low temperature losses in detail. It seems likely to us that they are

related to the phase transition observed in this temperature range by Menyuk and Dwight.[7]

IV. CONCLUSION

We conclude that the bulk of the losses due to Fe^{++} ions in ferrites are accounted for by the slow relaxation theory discussed in references 1, 2, and 3. This implies that the magnetic moments of the Fe^{++} ions are more tightly coupled to the magnetic lattice than to the crystal lattice at all relevant temperatures. There is, however, some evidence that this theory is an approximation and that the properties of the Fe^{++} ions deviate from it to an extent which, while small, is nevertheless observable.

We also conclude that there is more than one anisotropic loss in the ferrite investigated here, and the simple theory discussed in this work describes each separately, but does not explain why there is more than one. This does not change our conclusion, however, that the bulk of the losses associated with Fe^{++} ions are due to a mechanism for which the assumptions given by Eq. (1) are valid.

Finally, an added argument for our conclusion is that the Curie temperatures for the compounds FeO, Fe_2O_3, and Fe_3O_4 all lead one to expect exchange frequencies ω_{AB} in the compound we have studied which are too large to give $\omega_{AB}\tau=1$ for any of the τ's deduced here in the relevant range of temperature.

The authors wish to express their gratitude to J. F. Dillon, Jr., C. Herring, and R. C. LeCraw for critical comments on the manuscript, and S. Geller for an instructive conversation.

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PHYSICAL REVIEW VOLUME 127, NUMBER 5 SEPTEMBER 1, 1962

Annealing of Electron-Irradiated GaAs†

L. W. AUKERMAN AND R. D. GRAFT*
Battelle Memorial Institute, Columbus, Ohio
(Received April 23, 1962)

The annealing behavior of n-type GaAs irradiated at room temperature with 1-MeV electrons has been investigated. The fraction f of the defects remaining after annealing for a time t at an elevated temperature, decays according to the relationship, $f=a\exp(-\lambda_1 t)+(1-a)\exp(-\lambda_2 t)$. The rate constants λ_1 for various specimens annealed at different temperatures obey the Arrhenius relationship, giving an activation energy of 1.1 ± 0.05 eV. λ_1 appears to be an intrinsic property of n-type GaAs. λ_2, on the other hand, is dependent on the carrier density, i.e., the annealing is influenced by the position of the Fermi level. The recovery of p-type specimens is qualitatively different than that of n type. Some preliminary results concerning the effect of irradiation on electrical properties are also included.

INTRODUCTION

ANNEALING experiments carried out with irradiated metals have proven to be of considerable value in the interpretation of the type of damage introduced and the kinetics of its recovery.[1,2] Although a number of annealing studies have also been performed with various semiconductors, it does not appear that the details of the recovery of vacancies and interstitials have been completely worked out for any semiconducting material. The recovery of semiconductors may differ considerably from that of metals because of their relatively open lattice structure and different bonding. Furthermore, the position of the Fermi level may have a considerable effect on the annealing behavior of semiconductors.[3–5]

The recovery of compound semiconductors having the zinc-blende structure may be quite different from that of the elemental semiconductors, germanium and silicon. The variety of primordial defects is greater for compounds and the diffusion of a vacancy is, in all cases investigated so far, confined to a given sublattice.[6–8]

This paper is primarily concerned with the recovery of defects produced in GaAs, a semiconductor of the zinc-blende structure, by irradiation at room temperature with electrons of approximately 1-MeV energy. Ideally some irradiations should have been conducted at a much lower temperature, since annealing processes have been observed at temperatures well below room temperature in other semiconductors such as ger-

† This work was supported by the Aeronautical Research Laboratory, U. S. Air Force.
* Present address: North American Aviation Inc., Columbus, Ohio.
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