Internal Magnetic Fields in Manganese-Tin Alloys*

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The hyperfine fields at the tin sites in two manganese-tin alloys have been studied as a function of temperature to above the Curie points. In addition to the Zeeman splittings, observed and analyzed previously, a possible quadrupole interaction of about 27 Mc/sec is observed in Mn_2Sn. In Mn_4Sn the hyperfine field is small and negative, about -45 koe; in Mn_2Sn it is large and positive, about $+200$ koe. As in the case of the pure ferromagnetic transition elements, it seems necessary to invoke a positive term associated with conduction-electron polarization and a negative one arising from core polarization to explain these results.

THE ferromagnetic alloys of manganese and tin, which were used previously[1] in observing the Zeeman splitting of the nuclear levels of Sn^{119} by means of resonant absorption,[2] have now been studied more extensively to determine the nature of the internal magnetic field at the tin nucleus. The magnitude of the field has been measured as a function of temperature, and the measurements have been carried above the Curie point in order to observe possible quadrupole or other interactions in the absence of complications produced by magnetic splitting. In addition, the sign of the field in each alloy was established by observing the change in the hyperfine structure on application of a large external magnetic field, as in our earlier work with iron.[3]

Except as noted below, the experimental technique was the same as used in I. In Fig. 1 are shown measurements on Mn_4Sn at several temperatures from room temperature to above the Curie point at about 150°C.[4] For these observations the Mn_4Sn absorbing sample was clamped in vacuum in a frame which was warmed by an electrically heated coil of tungsten wire. The temperature was measured by a thermocouple in contact with the absorber. The Sn^{119} source, which emits an unsplit line, was maintained at the temperature of liquid nitrogen. It will be recalled from I that the basic resonant absorption spectrum for Mn_4Sn (with unsplit Sn source) consists of a doublet, each member of which is an unresolved triplet. The doublet separation is approximately equal to the magnetic splitting of the ground state. In Fig. 1 we can see this splitting decrease

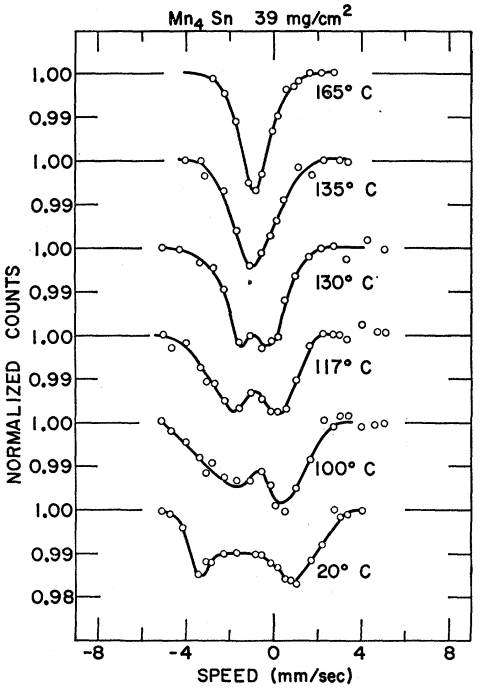

FIG. 1. Resonant absorption in Mn_4Sn, with a metallic Sn^{119} source at 77°K, for various absorber temperatures above and below the Curie point. Absorber thickness is 39 mg/cm².

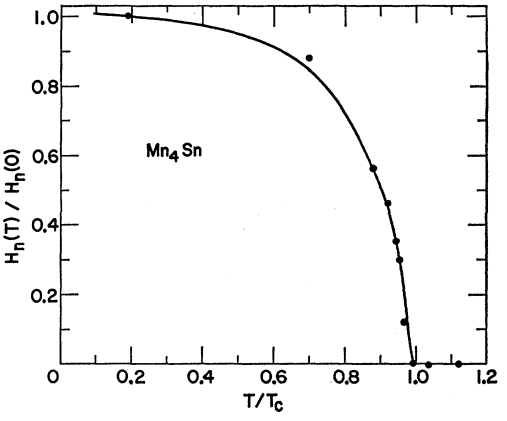

FIG. 2. Temperature variation of the internal field at the tin nucleus in Mn_4Sn. A Curie temperature T_c of 423°K has been assumed. Data taken from Fig. 1.

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[1] S. S. Hanna, L. Meyer-Schützmeister, R. S. Preston, and D. H. Vincent, Phys. Rev. **120**, 2211 (1960), hereafter referred to as I.

[2] R. L. Mössbauer, Z. Physik **151**, 124 (1958).

[3] S. S. Hanna, J. Heberle, G. J. Perlow, R. S. Preston, and D. H. Vincent, Phys. Rev. Letters **4**, 513 (1960).

[4] H. H. Potter, Phil. Mag. **12**, 261 (1931). The Curie temperature is given as 178°C by Ochsenfeld (reference 5). We continue to call this alloy Mn_4Sn in accordance with much of the literature. However, the structure is close-packed hexagonal of the Ni_3Sn type (DO_{19}). Actually, single phase samples appear to have a composition intermediate between Mn_3Sn and Mn_4Sn. We are greatly indebted to M. V. Nevitt for this information.

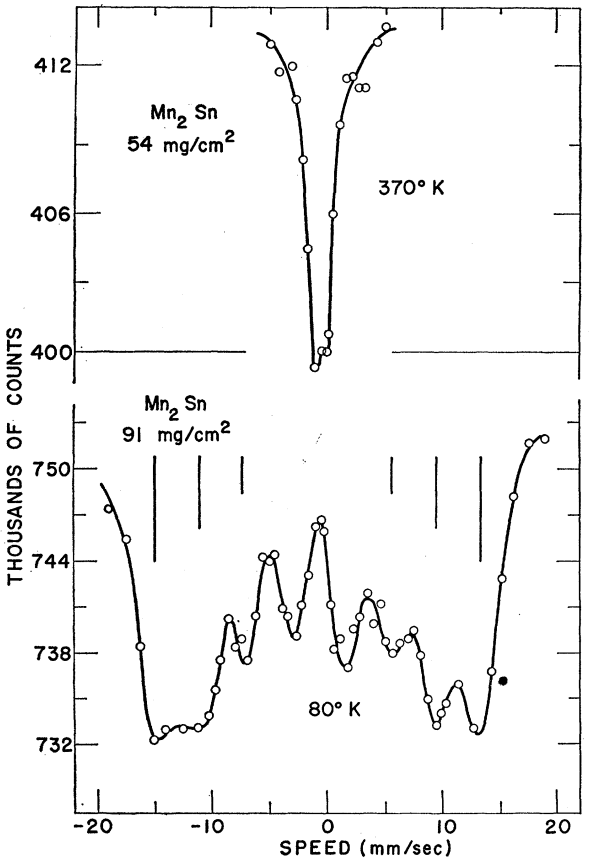

FIG. 3. Resonant absorption in Mn_2Sn, with a metallic Sn^{119} source at 77°K, at absorber temperatures below and above the Curie point. At 370°K the absorber thickness is 54 mg/cm²; at 80°K it is 91 mg/cm².

and then vanish as the temperature is raised to the Curie point. At these relatively high temperatures the absorption is very small and high precision has not been achieved in the data. The temperature variation of the internal field, as obtained from these and similar measurements, is displayed in Fig. 2. The data are normalized to the point obtained in I at the temperature of liquid nitrogen. The solid curve in the figure is a theoretical Weiss curve which is in rather good qualitative agreement with the experimental points. The value of the field at 0°K is estimated to be roughly 45 koe.

In Fig. 3 the absorption spectrum of Mn_2Sn is shown at two temperatures, one well below and the other well above the Curie point at −11°C.[5] At the lower temperature one observes the Zeeman spectrum analyzed in I. The value of the internal field at 0°K is estimated to be about 200 koe. Above the Curie point the spectrum collapses into a strong central absorption. Actually there is possibly a doublet structure in this central line as shown on an expanded velocity scale in Fig. 4. This structure is not strongly temperature dependent and would correspond to a quadrupole splitting of about 10^{-7} ev or 27 Mc/sec.

To obtain the sign of the internal field in these alloys, the powder sample, deposited on beryllium (0.010 in. thick), was clamped between two pieces of Lucite (each $\frac{1}{16}$ in. thick) and mounted in the gap ($\frac{1}{4}$ in.) of an electromagnet capable of producing fields up to 20 koe. A 0.001-in. foil of Pd was also inserted to reduce the 25-kev x ray from tin. The magnetic splittings in the absorption spectrum were then compared with the field off and on. Because of the small aperture provided by the absorber in the gap it was desirable in obtaining the absorption spectra to have the source oscillate as close as possible to the absorber in order to increase the counting rate. Since it was essential to keep the source cold, it was mounted in vacuum on a horizontal copper bar attached to a horizontal reservoir of liquid nitrogen. With this arrangement it was possible to bring the source to within about 1 in. of the absorber mounted vertically in the gap. The value of the fringing field at the average position of the source was about one sixth the field in the gap.

In the case of Mn_4Sn the measurements could be carried out with the absorber at room temperature, at which temperature the internal field at the tin nucleus has a value of about 40 koe.[1] Relative to this field the

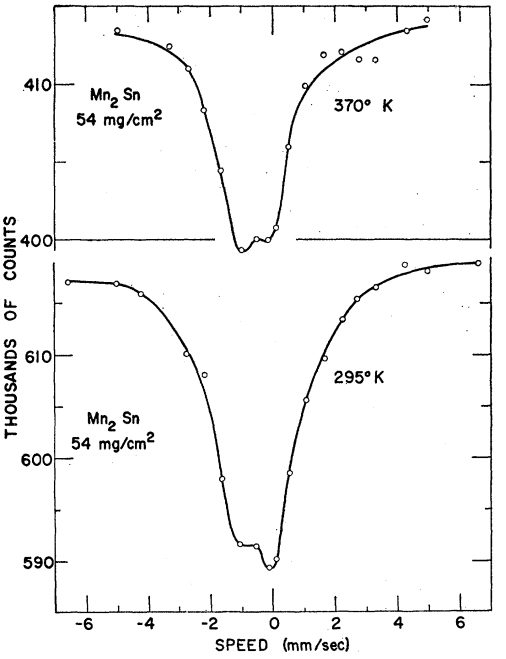

FIG. 4. Resonant absorption in Mn_2Sn, with a metallic Sn^{119} source at 77°K, at two absorber temperatures above the Curie point. The velocity scale is expanded over that in Fig. 3. Absorber thickness is 54 mg/cm².

[5] C. Guillaud, thesis, Strasbourg, 1943; quoted in R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., Princeton, New Jersey), p. 340; R. Ochsenfeld, Z. Metallkunde 49, 472 (1958). This alloy is reported to have a structure of the filled NiAs type, W. Hume-Rothery and G. V. Raynor, *The Structure of Metals and Alloys* (The Institute of Metals, London, England).

applied external field of about 17 koe should produce an easily detectible shift. The observations are shown in Fig. 5. On application of the external field the doublet separation is seen to decrease. Hence the internal field at the nucleus in Mn_4Sn is negative. The amount of the shift is compatible with the linear relation,

$$H_n = H_{n0} - H_{\text{ext}},$$

where H_n and H_{n0} are the hyperfine fields with and without the external field H_{ext}.

In the case of Mn_2Sn it was necessary to cool the absorber below the Curie point (−11°C) while keeping it in the gap of the electromagnet. To produce a convenient internal field of about 40 koe the absorber was maintained at a temperature of about −23°C. This was accomplished by allowing a stream of nitrogen gas, cooled by passage through a coil immersed in liquid nitrogen, to strike each side of the Lucite holder containing the absorber. It was found that the temperature, measured with a thermocouple, could be held constant to within about 1° by carefully regulating the stream of cold nitrogen gas. It was necessary, however, to enclose the complete assembly (source, absorber, and pole pieces) in a plastic sheet in order to prevent moisture from condensing on the cold surfaces. The measurements were made by alternating many runs with field on and field off. The final averages are shown in Fig. 6. In this case the doublet separation is seen to increase on application of the field. Hence the hyperfine field at the tin nucleus in Mn_2Sn is *positive*. The amount

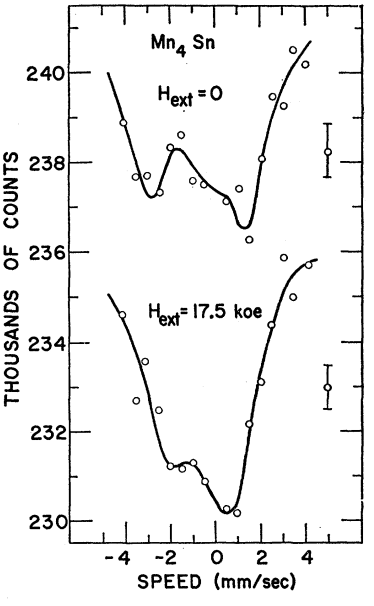

FIG. 5. Resonant absorption in Mn_4Sn at room temperature (~300°K) without an external magnetic field (above) and with an applied field of 17.5 koe (below). The splitting is decreased by application of the field. Absorber thickness is 42 mg/cm². Source temperature is 77°K.

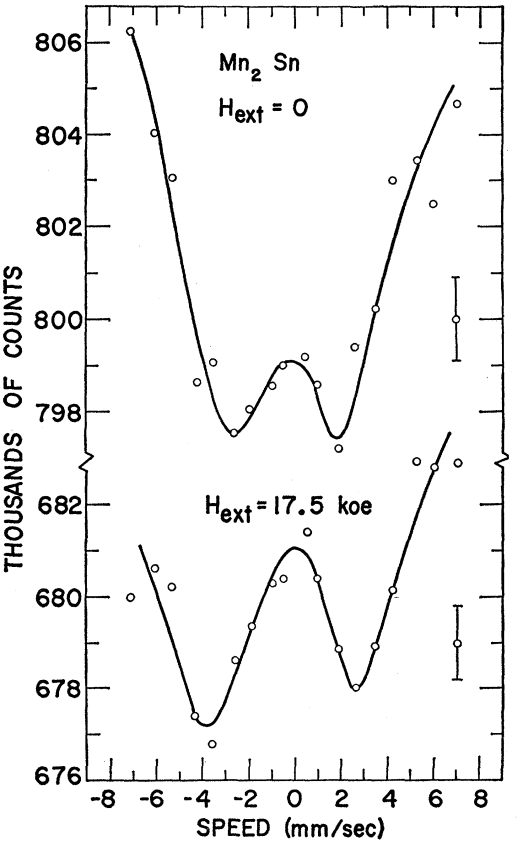

FIG. 6. Resonant absorption in Mn_2Sn at approximately 250°K without an external magnetic field (above) and with an applied field of 17.5 koe (below). The splitting is increased by application of the field. Absorber thickness is 45 mg/cm². Source temperature is 77°K.

of shift is compatible with the relation,

$$H_n = H_{n0} + H_{\text{ext}}.$$

Thus, a possible demagnetizing effect of the applied field in the sample is not noticeable in the above measurements.

Since the hyperfine field is large and negative (~−300 koe) in the pure ferromagnetic transition elements,[3,6,7] it is of considerable interest to find such a large positive field (+200 koe) at the tin site in the case of Mn_2Sn. Moreover, this field is very sensitive to the Mn:Sn ratio, since it changes sign in going to Mn_4Sn. It is significant, perhaps, that the saturation magnetization is some four times as great in Mn_2Sn as in Mn_4Sn.[4] The hyperfine field produced by the conduction electrons is given by Marshall[8] in the form

$$H_c = (8\pi/3)n|\psi(0)|^2\mu p,$$

[6] A. C. Gossard and A. M. Portis, Phys. Rev. Letters **3**, 164 (1959).

[7] S. S. Hanna, J. Heberle, C. Littlejohn, G. J. Perlow, R. S. Preston, and D. H. Vincent, Phys. Rev. Letters **4**, 177 (1960).

[8] W. Marshall, Phys. Rev. **110**, 1280 (1958).

where n is the number of conduction electrons per atom, $|\psi(0)|^2$ is the probability density of a conduction electron at the nucleus, μ is the Bohr magneton, and p is the polarization of the conduction electrons. It would appear that $n|\psi(0)|^2$ is roughly the same in the two alloys, since they show about the same isomer shift[9] (see Figs. 1 and 3).[9a] If, on the other hand, the polarization of conduction electrons (produced by the adjacent magnetic electrons) increases with saturation magnetization, then the polarization and so also H_c is greater numerically in Mn_2Sn than in Mn_4Sn. The simplest explanation of the large positive field in Mn_2Sn is that H_c is a *positive* field.

As for the pure transition elements,[3,10,11] it is necessary to postulate, in addition to H_c, the presence of a negative field, presumably associated with polarization of the core electrons of tin. In Mn_4Sn this field predominates. That this field is smaller, if different at all, in Mn_2Sn is consistent with the fact that the Weiss field is smaller, since the Curie temperature is lower and the magnetization larger in Mn_2Sn than in Mn_4Sn.

These effects observed in the manganese-tin alloys are somewhat analogous to those obtained by Boyle *et al.*[12] in dilute solutions of tin in the ferromagnetic transition elements. It is gratifying that essentially the same mechanisms[12] can be invoked to explain qualitatively the observations on all these tin alloys.

[9] O. C. Kistner and A. W. Sunyar, Phys. Rev. Letters **4**, 412 (1960).

[9a] *Note added in proof.* We are indebted to V. Jaccarino for pointing out that equality of the isomer shifts does not necessarily insure the above argument, since the polarization effect is localized at the top of the conduction band.

[10] D. A. Goodings and V. Heine, Phys. Rev. Letters **5**, 370 (1960).

[11] A. J. Freeman and R. E. Watson, Phys. Rev. Letters **5**, 498 (1960).

[12] A. J. F. Boyle, D. St. P. Bunbury, and C. Edwards, Phys. Rev. Letters **5**, 553 (1960).

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Pressure Effect on Vacancy Migration Rate in Gold*†

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The effect of hydrostatic pressures up to 10 000 kg/cm² on the annealing rate of vacancies quenched in gold is studied. High-purity gold wires are quenched from 700°C, trapping in the equilibrium concentration of vacancies at that temperature. The vacancies are then observed to anneal out in the vicinity of room temperature at various pressures by observing the decay of the quench-induced residual resistance increase. A simple relation for the temperature dependence of the annealing rate is derived, assuming a random distribution of vacancies and vacancy sinks. By applying thermodynamic relations to the expression for the vacancy annealing rate, a volume of motion is derived in terms of the experimentally determined pressure effect on the annealing rate. For gold, the motional volume is found to be 1.50 ± 0.14 cm³/mole compared with the atomic volume of 10.2 cm³/mole. A hard-spheres model for the jump process predicts about a one atomic volume increase of the lattice for the saddle-point configuration as well as a one atomic volume increase when a vacancy is formed. Many theoretical calculations of the lattice distortion around a vacancy and indirect experimental measurements of the volume change of the lattice on forming a vacancy indicate that there is considerable relaxation of the neighboring atoms about a vacancy. These results are used to explain the small value of the motional volume. Activation volumes derived from measurements of the effect of pressure on the rate of self-diffusion are seen to be consistent with the present experimental vlue.

I. INTRODUCTION

THE annealing of lattice vacancies quenched in a close-packed metal is closely related to the self-diffusion process. In the quenching technique, a supersaturation of vacancies is trapped in the lattice by rapidly cooling it from elevated temperatures and then is allowed to reach equilibrium at lower temperatures. The presence of these quenched-in vacancies is determined by the increase in the residual resistance of the lattice which they produce. Thus, the formation and motion of the vacancies can be observed separately. The sum of the energies of formation and of motion of vacancies quenched in various metals is generally in good agreement with self-diffusion activation energies measured for these metals by the radioactive tracer technique. Since most theories of diffusion treat the formation and motion of the defect separately, the quenching technique permits a more direct comparison of experiment with theory than is possible with tracer measurements.

The jump of an atom into a neighboring vacant site cannot be accomplished by a simple shear of the barrier atoms. Some dilatation of the lattice must occur to permit the interchange. The purpose of the present experiment is to determine the volume change of the

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