However, the theoretical situation is unclear with respect to the possibility of first-order transitions. The theory presented by Wagner and Swift[13] does not predict a first-order transition, whereas the model of Baker and Essam[14] exhibits a first-order transition related to a thermal instablity ($1/C_p < 0$). In the latter case, κ_T attains its upper bound of $3/2p$ at the point of instability. Since this value is very large at low pressures, it would be quite difficult to distinguish experimentally between this transition and one due to a mechanical instability. Although the Baker-Essam model has been applied quite successfully to the analysis of 1-atm data for β-brass, it is not yet clear whether it can account for a rapid change in the character of a transition with pressure.

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†Present address: Department of Chemistry, State University of New York, Stony Brook, N. Y.

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Hyperfine Field at the Tin Sites in the Heusler Alloy Ni_2MnSn†

W. Leiper, D. J. W. Geldart, and P. J. Pothier
Department of Physics, Dalhousie University, Halifax, Nova Scotia, Canada
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The hyperfine field H(Sn) at the tin sites in Ni_2MnSn has been measured by means of the Mössbauer effect at 300 and 77 °K. The results, which are independent of heat treatment, have been extrapolated to 0 °K to give a saturation field of $\pm 93 \pm 3$ kOe, in good agreement with a previous nuclear-magnetic-resonance measurement by Shinohara. H(Sn) has been calculated using the virtual-bound-state model, for a range of parameters of the theory. With the electronic ξ factor taken as 0.04 and the magnetic moment per Mn ion as $4.0 \pm 0.1 \mu_B$, agreement with experiment is obtained if the d-level occupation at Ni sites is 8.6.

I. INTRODUCTION

Heusler alloys are ternary intermetallic compounds of stoichiometric composition X_2YZ. The structure is cubic, with X ions at the cube corners and Y and Z ions occupying body centers of successive cubes. The study of Heusler alloys is of interest as it yields information concerning the electronic structure and related properties of concentrated magnetic alloys. In this paper we report the result of an investigation of the hyperfine field H(Sn) at the tin sites in the ferromagnetic Heusler alloy Ni_2MnSn.

H(Sn) in Ni_2MnSn has been measured by Kuz'min, Ibraimov, and Zhdanov[1] as ± 70.5 kOe at 77 °K by means of the Mössbauer effect. The hyperfine structure in the Mössbauer spectrum was not resolved in this measurement and Kuz'min *et al.* calculated H(Sn) by assuming that the spectrum obtained for Ni_2MnSn was similar in character to the spectra of Co_2MnSn for which, by varying the heat treatment, they got both resolved and unresolved

hyperfine structure. However, their result for H(Sn) in Co_2MnSn does not agree with the values obtained by other workers.[2,3]

Shinohara[2] employed the spin-echo technique to measure nuclear magnetic resonances in Ni_2MnSn. His result for H(Sn) was ± 97.0 kOe at 0 °K and he found that H(Sn) was independent of the heat treatment given to the sample.

A recent Mössbauer measurement by Segnan and Ferrando[4] on Ni_2MnSn gave a value for H(Sn) of ± 45 kOe at room temperature. The Curie temperature[5] of Ni_2MnSn is 344 °K so that considerable uncertainties are involved in extrapolating Segnan's result to 0 °K to obtain the saturation field strength.

The methods by which the samples were prepared and H(Sn) measured are discussed in Sec. II. The experimental result and a comparison with previous measurements are given in Sec. III. Section IV consists of a discussion of the way in which the present result can be related to the electronic structure of Ni_2MnSn and Sec. V contains a summary.

II. EXPERIMENTAL PROCEDURES

The Ni_2MnSn samples were prepared by mixing tin shot (99.999% purity),[6] nickel wire (99.998% purity),[6] and manganese broken cathodes (99.99% purity)[7] in stoichiometric quantities in an alumina crucible, and heating to 1100 °C in an argon atmosphere to prevent loss of the more volatile components. In order to investigate heat-treatment effects the sample was then either cooled slowly or quenched into room-temperature Dow Corning DC 702 oil. One sample was annealed for 120 h at 850 °C, then slow cooled. The results were found to be independent of heat treatment.

X-ray powder diffraction analysis showed that the Ni_2MnSn had the cubic structure expected of Heusler alloys, and that the lattice parameter was 6.034 ± 0.005 Å in agreement with a previously reported value[2] for Ni_2MnSn.

Powder samples, 40 mg per cm^2 thick, were analyzed on a constant acceleration Mössbauer spectrometer[8] at both 300 and 77 °K, using a room-temperature barium stannate Sn^{119m} source.

A Co^{57} source in a copper matrix and a 0.0025-cm-thick iron foil was used to give six velocity calibration channels in the multichannel analyzer. The Mössbauer transducer was fitted with a pick-up coil which produced a signal proportional to the transducer velocity (the coil was used in a feedback loop to stabilize the velocity waveform). The signal from the coil was taken to a voltage to frequency converter and the output of the converter fed to the multichannel analyzer so that a calibration of the entire velocity axis was obtained.

III. RESULTS

The Mössbauer spectra taken at 300 and 77 °K are shown in Fig. 1. A computer program, involving a least-squares technique, was used to optimize the parameters of six Lorentzian shapes to give a fit to the low-temperature experimental points. The peak positions of the Lorentz curves which gave a best fit to the experimental data were used to calculate H(Sn) as ± 87 ± 2 kOe at 77 °K. A value of ± 45 ± 5 kOe was estimated from the experimental results for H(Sn) at 300 °K.

The values for H(Sn) agree well with both the nuclear-magnetic-resonance result[2] and the room-temperature Mössbauer measurement by Segnan *et al.*[4] The agreement between the latter result and the present one might be largely fortuitous since a measurement by Segnan *et al.*[4] of H(Sn) in the Heusler alloy Cu_2MnSn differs by an order of magnitude from values found in this laboratory[9] and from theoretical estimates.[10]

The results of Kuz'min *et al.*[1] disagree both in the magnitude of H(Sn) and in the effect of heat treatment. However, as they were unable to resolve the hyperfine structure in the Mössbauer spectrum and found that heat treatment had a considerable effect on their results, it seems likely that they had imperfect samples with a high degree of disorder.

IV. DISCUSSION

To compare with the theoretical values of Sn

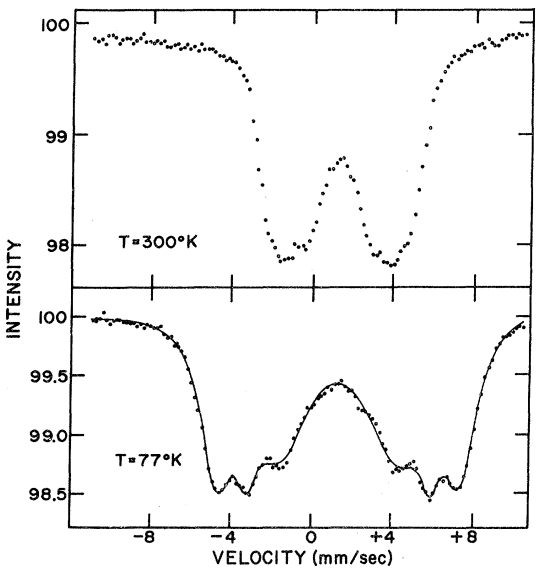

FIG. 1. Mössbauer absorption spectra for Ni_2MnSn at 300 and 77 °K. The source is Sn^{119m} at 300 °K. The solid line through the results at 77 °K is a computer fit to the spectrum.

hyperfine fields derived below, it is convenient to extrapolate our results to $T = 0\,^{\circ}\mathrm{K}$ to obtain the saturation field strength. Assuming that the field scales with the magnetization and that the latter follows the Bloch $T^{3/2}$ law, the saturation field strength is found to be 93 ± 3 kOe. Since the Curie point of Ni_2MnSn is rather low, a rough independent check on the saturation field was made by considering the internal field to be proportional to a Brillouin function for spin 2. The result obtained was in close agreement with that of the Bloch $T^{3/2}$ law.

First-principles calculations of hyperfine fields in the Heusler alloys are very difficult and have not been attempted. We have used the semiphenomenological virtual-bound-state model, first applied to Heusler alloys by Caroli and Blandin,[11] which has had considerable success. In the case of fields at the sites of polyvalent ions, however, a modification proposed by Geldart and Ganguly[10] is important when estimating s-wave character of conduction electron density. The above work has been described in the literature and only an outline of its application to Ni_2MnSn will be given here.

The effective field at the Sn sites is assumed to be given by the conduction electron spin polarization induced by Mn ions. Neglecting interference between Mn ions and summing over all Mn neighbors to obtain the total polarization at the Sn sites yields[12]

$$H(\mathrm{Sn}) = \xi \frac{\Omega_0 hc\, a(s)}{2 g_N \mu_N} \sum_n \rho_0(\vec{R}_{0_n}) , \qquad (1)$$

where $a(s)$ is the hyperfine constant of the free Sn atom and ξ is a factor specifying the s-wave character of Fermi-surface conduction electrons at Sn sites in the alloy. With these ionic structure factors taken into account, $\rho_0(\vec{R}_{0_n})$ is then the spin polarization which would be produced by a Mn ion in a free-electron gas of the same Fermi energy as the Heusler alloy. Ω_0 is the average volume per ion and the rest of the notation is standard.

To obtain a reasonable value for ξ, we note that $\xi \simeq 0.044$ for Sn ions in the similar Heusler alloy Cu_2MnSn yields agreement between theory[10] and the two independent experimental results of Chekin, Danilenko, and Kaplienko[13] and of Leiper.[9] Because Cu ions tend to produce a simpler conduction band than do Ni ions we expect the electronic wave functions (of the Fermi energy) at Sn sites to have slightly larger s-wave components in Cu_2MnSn than in Ni_2MnSn. Accordingly, $\xi = 0.04$ was used in the present calculation.

We must next specify the number of d electrons at Mn and Ni sites. These parameters determine the amplitude and phase variation of the spin polarization $\rho_0(\vec{R}_{0_n})$ in Eq. (1). Complete spin splitting is expected at Mn sites just as in similar Heusler alloys[10,11] so $Z_d\uparrow(\mathrm{Mn}) = 5$. We have taken the magnetic moment M per Mn ion as $4.0 \pm 0.1\ \mu_B$ in this alloy.[2,5] The Ni ions carry no moment[5] so that $Z_d\uparrow(\mathrm{Ni}) = Z_d\downarrow(\mathrm{Ni})$. The d-level occupation at Ni sites can then be expressed in terms of $Z_d^{\mathrm{tot}}(\mathrm{Ni}) = Z_d\uparrow(\mathrm{Ni}) + Z_d\downarrow(\mathrm{Ni})$, which is expected to be of order 9 as in the case of dilute alloys of Ni in the noble metals.[14,15] Finally, the remaining $7 - Z_d^{\mathrm{tot}}(\mathrm{Mn})$ and $10 - Z_d^{\mathrm{tot}}(\mathrm{Ni})$ electrons plus 4 electrons from each Sn ion are assumed to form a simple conduction band of sp type. The Fermi energy of the conduction band is obtained from the density of sp-type electrons in the usual way and $\rho_0(\vec{R}_{0_n})$ is then completely determined.

The lattice sum in Eq. (1) was evaluated on a computer for a range of values of the parameters $Z_d^{\mathrm{tot}}(\mathrm{Ni})$ and M. The results are given in Fig. 2 for the case $\xi = 0.040$.

Although the general range of the parameters of the theory can be estimated, this still leaves considerable imprecision in the magnitude of the predicted saturation field. This is mainly due to the sensitivity of the lattice sum in Eq. (1) to variations in $Z_d^{\mathrm{tot}}(\mathrm{Ni})$. Using $M = 4.0 \pm 0.1\ \mu_B$ and $\xi = 0.04$ as indicated above, agreement with the experimental value of the saturation hyperfine field, $H(\mathrm{Sn}) = \pm 93$ kOe, is obtained for $Z_d^{\mathrm{tot}}(\mathrm{Ni}) = 8.6$ which is close to the value obtained in dilute alloys.[13,14] The sign of $H(\mathrm{Sn})$ was not determined in this experiment but is predicted to be positive by the theory, in terms of the standard sign convention.[16]

V. SUMMARY

We have made Mössbauer measurements of the

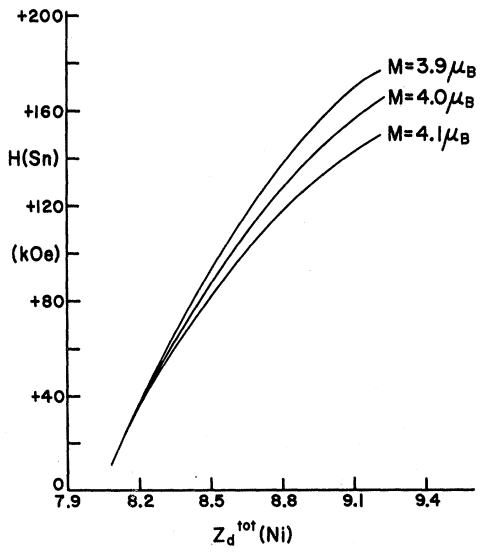

FIG. 2. Calculated values for the hyperfine field at the tin sites in Ni_2MnSn as a function of the magnetic moment per Mn ion and the d-level occupation at Ni sites.

hyperfine field H(Sn) at the tin sites in the ferromagnetic Heusler alloy Ni_2MnSn. The results at 300 and 77 °K were, respectively, $\pm 45 \pm 5$ and $\pm 87 \pm 2$ kOe. The Bloch $T^{3/2}$ law was used to extrapolate the results to 0 °K, to obtain a saturation field of $\pm 93 \pm 3$ kOe. This agrees with the result of Shinohara[2] who found H(Sn) = 97.0 kOe at 0 °K by observing nuclear magnetic resonances in Ni_2MnSn, using the spin-echo technique.

An extension of the virtual-bound-state, or resonance, model, first proposed by Caroli and Blandin,[11] was used to calculate H(Sn). The hyperfine field at the tin sites is considered to be due to the Fermi contact interaction between the spin polarization, induced in the conduction band by the Mn-ion-spin splitting, and the nuclear magnetic moments at the tin sites. The electronic ξ factor, which determines the reduction in s-wave character of the electronic wave functions at the Sn sites in going from a free atom to a metallic environment, was taken as $\xi = 0.04$. The magnetic moment per Mn ion, M, was taken from neutron-diffraction data[5] and thermomagnetic measurements[2] as $4.0 \pm 0.1\ \mu_B$. H(Sn) was then calculated for a range of values of the d-level occupation, Z_d^{tot}(Ni), at the Ni sites. The theoretical calculations were found to be sensitive to the value of Z_d^{tot}(Ni). Agreement with the experimental result was obtained for Z_d^{tot}(Ni) = 8.6.

Finally, it should be emphasized that although the values obtained for the parameters ξ and Z_d^{tot}(Ni) are reasonable in view of other experimental evidence, they are dependent upon the model which was used in the present calculation.

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Rare-Earth Spin-Disorder Resistivity and Spin-Orbit Coupling*

S. Legvold

Institute for Atomic Research and Department of Physics, Iowa State University, Ames, Iowa 50010

(Received 10 August 1970)

Without corrections for Fermi-surface effects, the total-spin-disorder electrical resistivity of heavy-rare-earth single crystals is accidentally proportional to $S(S+1)$ in the basal plane and to $(\lambda-1)^2J(J+1)$ in the c direction. When Fermi-surface effects are included, results show $(\lambda-1)^2J(J+1)$ dependence in both directions.

For some time it has been understood that the total-spin-disorder resistivity ($\rho_{m,sat}$) in the heavy-rare-earth metals should be proportional to $(\lambda-1)^2J(J+1)$ because of spin-orbit coupling[1-3]; here J is the total angular-momentum quantum number and λ is the Landé factor. While analyzing recent electrical-resistivity measurements[4-9] in rare-earth single crystals, we looked into the total-spin-disorder resistivity in different crystallographic (hcp) directions and found a surprising result which we report here.

The electrical resistivity in the basal-plane direction for each metal showed a nearly linear behavior in the paramagnetic range so it was easy to extrapolate this back to the resistivity axis, subtract the residual resistivity from the intercept