PHYSICAL REVIEW B

CONDENSED MATTER

THIRD SERIES, VOLUME 26, NUMBER 11 1 DECEMBER 1982

Mössbauer-effect study of Sn-impurity-site hyperfine fields in the Heusler alloys Co_2MnZ (Z = Al,Ga,Si,Ge,Sn)

R. A. Dunlap and D. F. Jones

Department of Physics, Dalhousie University, Halifax, Nova Scotia B3H 3J5, Canada

(Received 23 July 1982)

The hyperfine field at the Sn site in the Heusler alloys $Co_2MnZ_{0.98}Sn_{0.02}$, for Z = Al, Ga, Si, Ge, and Sn, was measured using the Mössbauer effect. Values of +40.5, +35.3, −15.6, +6.2, and +102 kOe were obtained for the five alloys, respectively. Co_2MnAl and Co_2MnGa both have magnetic moments of approximately $0.5\mu_B$/Co and $3.0\mu_B$/Mn as well as similar lattice parameters. It is therefore reasonable that the Sn-impurity-site hyperfine fields are similar in the two alloys. The $Co_2Mn(Si,Ge,Sn)$ series of alloys all have moments of approximately $0.75\mu_B$/Co and $3.6\mu_B$/Mn. The large variation in field in these alloys can be attributed to differences in the lattice parameters. Theoretical predictions of Jena and Geldart, and of Blandin and Campbell, and the volume-overlap model of Stearns, are applied to these alloys. Neither the model of Jena and Geldart nor the model of Blandin and Campbell is in satisfactory agreement with our experimental results. Numerical results for the volume overlap cannot be attained because of the lack of experimental results for the Co-based Heusler alloys. Trends predicted by this model are discussed in terms of the results obtained in this study.

I. INTRODUCTION

Heusler alloys have made a unique contribution to the understanding of nonmagnetic-site hyperfine fields in ferromagnets. These alloys are of the chemical composition X_2YZ or XYZ and have the $L2_1$ or $C1_b$ crystal structure, respectively. The magnetic properties of these alloys arise from magnetic moments on transition-metal atoms located on either the X or Y site. Most commonly the moments on the X sites are associated with Co atoms while the moments on the Y sites are associated with Mn atoms.[1–3] The alloys of the form Co_2MnZ offer the unique opportunity to study Heusler alloys in which magnetic moments exist on two inequivalent lattice sites. The measurement of hyperfine fields in these alloys with different Z atoms allows for the study of the relationship between these fields and quantities such as lattice parameter, magnetic moments, and the valence of the Z atom. Fields in different alloys are most easily compared if the probe nucleus remains the same. Neither the Co- nor the Mn-site fields in these alloys are suitable because of the difficulty in interpreting hyperfine fields at sites which have magnetic moments associated with them. In this work the alloys Co_2MnZ (Z = Al,Ga,Si,Ge,Sn) have been prepared with 2% Sn substituted into the Z site. The Sn hyperfine field has been measured using Mössbauer effect and the results are compared with the predictions of current theories. The structural properties have also been investigated using x-ray diffraction.

II. EXPERIMENTAL METHODS

Alloys of the composition $Co_2MnZ_{0.98}Sn_{0.02}$, with Z = Al, Ga, Si, Ge, and Sn, were prepared by induction melting the constituents followed by grinding. The resulting powders were annealed in quartz ampoules under an atmosphere of argon for

TABLE I. Measured lattice parameters and Sn hyperfine fields in the Heusler alloys $Co_2MnZ_{0.98}Sn_{0.02}$.

Alloy (Z)	a (Å)[a]	H(Sn) (kOe) This work	Other work
Al	5.754(5)	+40.5(5)	
Ga	5.772	+35.3(2)	
Si	5.654	−15.6(2)[b]	−14.3(4)[d]
Ge	5.745	+6.2(5)[b]	+10.5(5)[d]
Sn	6.000	+102(3)[c]	+105(1)[e]

[a]This work.
[b]Sign determined by Ref. 10.
[c]Sign determined by Ref. 8.
[d]Reference 10.
[e]Reference 9.

72 h at 800 °C and quenched in ice water.

Room-temperature x-ray diffraction measurements were made on a Philips powder diffractometer using Cu $K\alpha$ radiation. These measurements ensured that each of the samples was of the $L2_1$ structure[4] and yielded the lattice parameters given in Table I. These lattice parameters are in good agreement with those previously reported by Webster[3] for the Co_2MnZ alloys. X-ray diffraction measurements by Webster[3] on Co_2MnAl indicated a large amount of preferential Mn-Al disorder. No disorder was apparent from the x-ray diffraction line intensities for our sample of $Co_2MnAl_{0.98}Sn_{0.02}$.

An attempt was also made to prepare an alloy of the composition $Co_2MnSb_{0.98}Sn_{0.02}$. X-ray diffraction measurements showed this alloy to be a mixture of two phases: a Heusler alloy intermediate between the $C1_b$ and $L2_1$ structures with a lattice parameter of 5.910 Å and a quantity of free Co. This is consistent with the results reported by Webster[3] for Co_2MnSb. Additional measurements on this alloy are not presented because of the uncertainty in the stoichiometry of the Heusler phase.

^{119}Sn Mössbauer measurements were made at 77 K using a $^{119}Ca^mSnO_3$ source and a conventional constant-acceleration spectrometer. These spectra were calibrated to the liquid-nitrogen temperature Sn hyperfine field of 102 kOe in Co_2MnSn.[4–6] The sign of the Sn field in $Co_2MnAl_{0.98}Sn_{0.02}$ and $Co_2MnGa_{0.98}Sn_{0.02}$ was measured in an external magnetic field of approximately 6 kG.

III. RESULTS

The ^{119}Sn Mössbauer spectra obtained at 77 K are shown in Fig. 1. With the exception of the spectrum for Co_2MnSn, the spectra were fitted using a conventional least-squares fitting routine. The Co_2MnSn spectrum was fitted using the Fourier expansion method of Window.[7] This method was used for this spectrum since it was previously shown to be suitable by Dunlap and Stroink[4] and their field value was used to calibrate the velocity scale in this work. The field in this case was taken to be the most probable field as given by the peak in the probability distribution. The details of this field distribution have been discussed previously by Dunlap and co-workers.[4,6] Fitting the Co_2MnSn spectrum using a conventional least-squares fitting method yielded a calibration which was consistent to within 2% of the value obtained from the Window method but yielded physically unrealistic line-intensity ratios as previously pointed out by Williams.[8,9] The values of the Sn fields obtained here are also given in Table I.

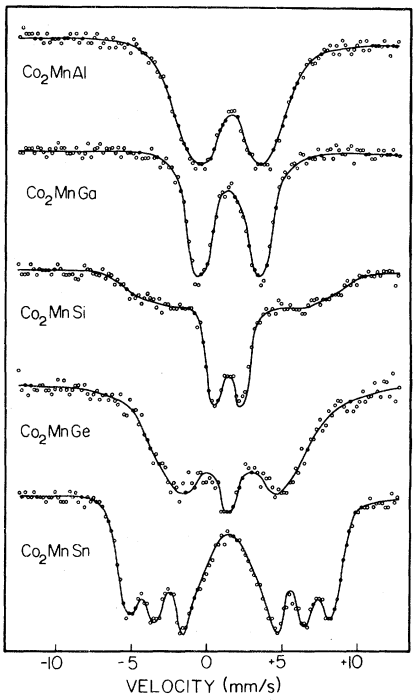

FIG. 1. ^{119}Sn Mössbauer-effect spectra at 77 K for $Co_2MnZ_{0.98}Sn_{0.02}$. Computer fits as discussed in the text are shown by the solid curves.

The measurements made in an applied field indicate that the Sn fields in $Co_2MnAl_{0.98}Sn_{0.02}$ and $Co_2MnGa_{0.98}Sn_{0.02}$ are both positive. The alloys $Co_2MnSi_{0.98}Sn_{0.02}$ and $Co_2MnGe_{0.98}Sn_{0.02}$ both show two Sn field components. On the basis of the measurements of Delyagin *et al.*[10] the component with the smaller splitting is presumably, in both

cases, the component due to Sn on the Z site in the Heusler structure. Delyagin *et al.*[10] have determined the Sn field to be negative in Co_2MnSi and positive in Co_2MnGe. The Sn fields obtained in this work for Co_2MnSi and Co_2MnGe are in good agreement with those reported previously.[10] The Sn field components with the larger splitting in the Co_2MnSi and Co_2MnGe spectra show field values of 84(1) and 61(1) kOe, respectively. The sign of these fields was not determined. These fields are possibly due to Sn located on the X sites in the Heusler structure. In the following section we deal only with the field at Sn nuclei located on the Heusler Z sites.

IV. DISCUSSION

The interpretation of nonmagnetic-site hyperfine fields in the Heusler alloys has been the subject of a good deal of controversy in recent years.[11–13] In particular, those alloys which contain Co appear to be difficult to describe theoretically.[10,11] In view of previous experimental results it seems clear that the hyperfine field systematics in these Co-based alloys can be quite different from the systematics in Heusler alloys which contain Mn as the only magnetic atoms.[10,11] The theory of Jena and Geldart (JG),[14] which has been used with some success in those Heusler alloys which contain Mn as the only magnetic atoms,[15] makes clearly incorrect predictions for the trends in Co-based Heusler alloys.[11] Our measurements here on Sn fields in the series $Co_2Mn(Si,Ge,Sn)$ show similar trends to those observed in our previous work on $Co_2Ti_{1-x}V_xSn$ and cannot be explained by the uniformly spin-split conduction-band picture of the JG theory. The theories[12,16] of Blandin and Campbell and Stearns[13,17,18] have been previously suggested to describe the magnetic behavior of Co_2MnSn.[19,20] The application of these two theories to the alloys studied here is discussed below.

A. Blandin-Campbell theory

It is customary to express the hyperfine field at a nonmagnetic impurity site in a ferromagnetic host as the sum of partial contributions from neighboring magnetic moments[10] as

$$H=\sum_i \mu(r_i)p(r_i)\ . \tag{1}$$

μ is the magnetic moment of an atom located at r_i and $p(r_i)$ is the reduced partial contribution to the hyperfine field at the probe nucleus. Blandin and Campbell (BC) have calculated[12,16,21] the $p(r_i)$ using an extension of the Ruderman-Kittel-Kasuya-Yosida interaction which takes into account perturbations in the conduction-electron density resulting from localized charge at the impurity atom. This assumes that the dominant mechanism responsible for the magnetic field at the nonmagnetic-site nucleus is the interaction between s-like conduction electrons and localized d electrons. The contributions to the hyperfine field are expressed in the form[16]

$$p(r_i)\alpha\frac{1}{r_i^3}\cos(2k_Fr_i+2\delta_0+\eta)\ . \tag{2}$$

k_F is the Fermi vector given in terms of the average number of conduction electrons per atom n_0 as

$$k_F=\frac{1}{a}(48\pi^2n_0)^{1/3}\ . \tag{3}$$

The $2\delta_0$ term accounts for the perturbations to the conduction-electron density from the effective charge of the impurity atom and is expressed

$$2\delta_0=\frac{\pi}{4}(Z_v-n_0)\ , \tag{4}$$

where Z_v is the valence state of the impurity atom. The preasymptotic factor η is generally taken to be $\pi/2$ for second-nearest-neighbor (e.g., Sn-Mn) interactions in the Heusler alloys.[16] For this work we use the preasymptotic factor with a radial dependence, $\eta=C/(k_Fr)$, suggested by Jena and Geldart.[22] The parameter C was found by normalizing η to the value of $\pi/2$ for the Sn-Mn distance for each lattice. The average number of conduction electrons has been expressed as[11]

$$n_0=\tfrac{1}{4}[2(L_{Co}-2D_{Co}+\mu_{Co}) +(L_{Mn}-2D_{Mn}+\mu_{Mn})+N_Z]\ , \tag{5}$$

where L_i is the number of outer-shell electrons and D_i is the number of spin-down outer electrons. N_Z is the number of electrons contributed to the conduction band by the Z element. It has been assumed that the Mn and Co atoms have 4.5 and 4.7 spin-down electrons, respectively, and that the group-III*a* and -IV*a* *sp* elements contribute 3 and 4 conduction electrons, respectively.[4,11] Table II gives values of the parameters necessary for the calculation of hyperfine fields in these alloys. Figure 2 shows the radial dependence of the reduced partial contribution to the hyperfine field for Sn impurity sites in Co_2MnAl. The locations of the Co and Mn nearest neighbors are shown in the figure. The radial dependence of $p(r_i)$ for the other alloys in this

TABLE II. Magnetic properties of the Co_2MnZ Heusler alloys.

Alloy	T_c (K)[a]	σ (emu/g)[a]	μ_{Co} (μ_B)[a]	μ_{Mn} (μ_B)[a]	n_o[b]	k_F (Å^{-1})[b]
Co_2MnAl	693	112.5	0.50	3.01	1.05	1.38
Co_2MnGa	694	94	0.52	3.01	1.06	1.38
Co_2MnSi	985	142	0.75	3.57	1.57	1.60
Co_2MnGe	905	118	0.75	3.61	1.58	1.58
Co_2MnSn	829	96	0.75	3.58	1.57	1.51

[a]Reference 3.
[b]This work; see text.

study is similar. Table III gives calculated values of the hyperfine field, H(Sn). Because of the number of unknown parameters involved in the calculation of H(Sn), the BC theory is not as useful for predicting the field in a particular alloy as it is for predicting trends in a series of alloys. For this reason the calculated field values given in Table III have been normalized to the value of + 102 kOe in Co_2MnSn. Values of the field predicted by the JG model[14,22,23] and similarly normalized are given in the table for comparison. As we have discussed previously[11] the JG theory seems inappropriate for describing the Co-based Heusler alloys which do not contain Mn and Table III suggests that this is also the case for those Co-based Heusler alloys which do contain Mn.

The values of the field obtained from the BC theory fail to show the proper trend in the Co_2Mn(Si,Ge,Sn) series. The theory, however, makes reasonable predictions for the fields in the Co_2Mn(Al,Ga) alloys.

The average number of conduction electrons per atom used here for Co_2Mn(Al,Ga) is consistent with Campbell's assumption[16] that this is about one electron per atom for the Heusler alloys. Because of the larger moments on the Co and Mn atoms in Co_2Mn(Si,Ge,Sn), the number of conduction electrons is necessarily larger. Görlich *et al.*[20] have suggested that n_0 is sufficiently difficult to estimate that it should be left as a free parameter to be determined by the theory. For the Co-based Heusler alloys which do not contain Mn, they obtain $n_0 \simeq 0.52$. In the alloys studied here we must account for the moment on the Mn. We cannot obtain values for n_o much less than 1.0 unless we assume, as suggested by Stearns,[18] that the *sp* elements contribute only a small number of conduction electrons. It is possible, by proper choice of n_o, to obtain reasonable agreement between the BC theory and our experimental results. However, it is not possible to do so by using consistent values of n_o for all the alloys. The difficulty in predicting the observed trends results from the relatively weak dependence of the sum of the partial contributions of the form of Eq. (2) on n_o. That is, it is not possible to predict the large field variations observed in the Co_2Mn(Si,Ge,Sn) series where this variation is presumed to be due only to changes in the lattice parameter.[10] This theory also fails to predict the proper field trend between Co_2MnAl and Co_2MnGe where the change is due predominantly to different magnetic moments rather than a change in the lattice parameter.

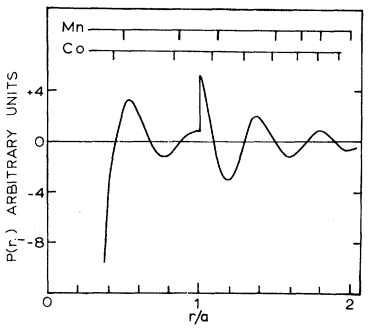

FIG. 2. Radial dependence of the reduced partial contribution to the Sn hyperfine field calculated using the BC theory for Co_2MnAl. Note that there is a change of a factor of 10 in the vertical scale at $r=a$. The location of the Mn and Co nearest neighbors are indicated in the figure.

TABLE III. Calculated BC and JG Sn hyperfine-field values in kOe.

Alloy	BC	JG
Co_2MnAl	+45	−30
Co_2MnGa	+44	−30
Co_2MnSi	+107	+245
Co_2MnGe	+109	+207
Co_2MnSn	+102	+102

B. Volume-overlap model

Stearns has suggested[13,17,18,24] that the magnetic properties of the Heusler alloys result from three interactions:

(1) An interaction between *s*-like conduction electrons and localized *d* electrons via Coulomb exchange and hybridization.

(2) A similar interaction between itinerant *d*-like electrons and localized *d* electrons.

(3) A superexchange interaction through the *sp* elements at the *Z* Heusler sites. Most previous models have treated only the *s-d* interaction, while Stearns has proposed that the *d-d* interaction is the dominant one. This picture leads to the calculation of hyperfine fields and impurity sites using the volume-overlap model. This assumes that the total-impurity-site hyperfine field may be expressed in terms of two contributions:

(1) A negative contribution due to the polarization of *s*-like conduction electrons of the host alloy. This remains unperturbed by the substitution of an impurity atom.

(2) A positive term due to the volume overlap between nonmagnetic and magnetic atoms. These two contributions, H_h and H_i, due to the host and the impurity, respectively, are considered to be separable and additive. Thus the total field at an impurity site of atomic number Z may be expressed as

$$H(Z)=H_h(Z)+H_i(Z) . \tag{6}$$

In contrast, charge perturbation models (e.g., BC and JG) assume that the host and impurity contributions to the hyperfine field are nonseparable. The host term in Eq. (6) is found to scale with the hyperfine coupling constants, $A(i)$. Thus, for a given host alloy, the host contributions at two impurity sites, Z and Z' are related by

$$H_h(Z)=H_h(Z')A(Z)/A(Z') . \tag{7}$$

The volume overlap term is given by

$$H_i(Z)=C[V(Z)-V_0]A(Z) . \tag{8}$$

The parameters C and V_0 are characteristic of the host matrix and $V(Z)$ is an atomic volume term for the impurity atom. This model, in principle, contains no "free parameters" in the sense that the BC and JG theories do. The values of the atomic coupling constants $A(i)$ have been calculated by a number of authors[25–27] and there is reasonable agreement on these. Each host material is characterized by the three parameters $H_h(Z')$, C, and V_0. These are customarily fitted for a particular host by using experimentally measured fields in that alloy. The Z' atom is chosen to be one in which $V(Z')<V_0$ and there is therefore no overlap term [i.e., $H_h(Z')=H(Z')$]. Stearns[18] has suggested Cd as an appropriate choice of Z'. The parameters C and V_0 may then be calculated from the measurement of two impurity fields in the same host for which the overlap term does exist. This theory is ideally suited to the prediction of hyperfine fields at a large number of different impurity sites in the same host alloy. For this reason it has most commonly been used for predicting impurity fields in Fe. Because of the large number of "fitted" parameters for a given host, the work presented here presents a more complex problem of applying Stearns's model, that in which the hyperfine field at the same impurity atom has been measured in a number of different hosts.

Unfortunately, impurity-site hyperfine fields in the Co-based Heusler alloys have not been reported to the extent that they have in the other Heusler alloys. Le Dang Khoi *et al.*[28] have measured the Si hyperfine field in Co_2MnSi to be ± 32 kOe. In terms of calculated atomic volumes, 12.1 $cm^3\,mole^{-1}$ for Si and 13.0 $cm^3\,mole^{-1}$ for Cd, we would expect the overlap term for Si to be zero. Stearns's model would therefore predict the sign of the Si field to be negative. In the absence of the overlap term we may relate the Si hyperfine field to the Cd field in the same Heusler host as

$$H(\mathrm{Cd})=H(\mathrm{Si})A(\mathrm{Cd})/A(\mathrm{Si}) \tag{9}$$

Using $A(\mathrm{Cd})/A(\mathrm{Si})=5.24$, as predicted by Campbell,[26] we find $H(\mathrm{Cd})=-168$ kOe in Co_2MnSi.

The calculation of C and V_0 for any of the Co-based Heusler hosts is not directly possible because of the lack of sufficient experimental measurements. It has been suggested, however, that these parameters for different Heusler alloys should scale as the lattice parameter.[29] It is not clear that this should necessarily be the case between alloys which have moments on the X sites and those which do not. It should, however, be a reasonable assumption for a series of Co-based Heusler alloys in which the moments remain essentially constant, i.e., $Co_2Mn(Si,Ge,Sn)$. Hence, in this series, as the lattice parameter increases the volume-overlap term in Eq. (6) should decrease. The observed increase in Sn impurity field with increasing lattice parameter for the $Co_2Mn(Si,Ge,Sn)$ series may be explained by this theory only if the host contribution is correspondingly more positive in alloys with larger lattice parameters. Since the Sn field in Co_2MnSn is

118 kOe more positive than the Sn field in Co_2MnSi, the Cd field in Co_2MnSn must be at least $118A(Cd)/A(Sn)=76$ kOe more positive than the Cd field in Co_2MnSi. Therefore, according to the volume-overlap theory, we would not expect a Cd field in Co_2MnSn which was less (more negative) than -92 kOe. This is in contrast to the BC theory which predicts that the Cd field in Co_2MnSn is only slightly more positive than the Cd field in Co_2MnSi. Thus the measurement of the Cd hyperfine field in Co_2MnSi and Co_2MnSn is of importance in determining the validity of the volume-overlap model for predicting fields in the Co-based Heusler alloys.

In conclusion we find that neither the JG nor the BC theories provide satisfactory predictions for the Sn hyperfine fields in the Co_2MnZ Heusler alloys. Numerical results for the volume-overlap model could not be obtained because of the lack of experimentally measured fields in the Co-based Heusler alloys. The measurement of Cd hyperfine fields in some of the alloys studied here could determine the validity of this model.

ACKNOWLEDGMENTS

The authors are most grateful to B. Fullerton for preparing the alloys. We are also appreciative of S. Ritcey and D. J. W. Geldart for many fruitful discussions. This work was supported by the Faculty of Graduate Studies, Dalhousie University, and a grant from the Natural Sciences and Engineering Research Council of Canada.

[1]C. C. M. Campbell, J. Phys. F 5, 1931 (1975).
[2]P. J. Webster and K. R. A. Ziebeck, J. Phys. Chem. Solids 34, 1647 (1973).
[3]P. J. Webster, J. Phys. Chem. Solids 32, 1221 (1971).
[4]R. A. Dunlap and G. Stroink, Can. J. Phys. 60, 909 (1982).
[5]J. S. Brooks, J. M. Williams, and P. J. Webster, J. Phys. D 6, 1403 (1973).
[6]R. A. Dunlap, R. H. March, and G. Stroink, Can. J. Phys. 59, 1577 (1981).
[7]B. Window, J. Phys. E 4, 401 (1971).
[8]J. M. Williams, J. Phys. C 2, 2037 (1969).
[9]J. M. Williams, J. Phys. C 1, 473 (1968).
[10]N. N. Delyagin, Y. D. Zonnenberg, V. I. Krylov, and V. I. Nesterov, Hyperfine Interact. 11, 65 (1981).
[11]R. A. Dunlap and G. Stroink, J. Appl. Phys. (in press).
[12]I. A. Campbell and I. Vincze, Phys. Rev. B 13, 4178 (1976).
[13]M. B. Stearns, Phys. Rev. B 8, 4383 (1973).
[14]P. Jena and D. J. W. Geldart, J. Magn. Magn. Mater. 8, 99 (1978).
[15]W. R. Mayo and R. A. Dunlap, J. Appl. Phys. (in press).
[16]I. A. Campbell and A. Blandin, J. Magn. Magn. Mater. 1, 1 (1975).
[17]M. B. Stearns, Phys. Rev. B 13, 4180 (1976).
[18]M. B. Stearns, J. Appl. Phys. 50, 2060 (1979).
[19]E. Uhl, J. Magn. Magn. Mater. 25, 221 (1981).
[20]E. A. Görlich, R. Kmeić, K. Latka, T. Matlak, K. Reubenbauer, A. Szytula, and K. Tomala, Phys. Status Solidi A 30, 765 (1975).
[21]A. Blandin and I. A. Campbell, Phys. Rev. Lett. 31, 51 (1973).
[22]P. Jena and D. J. W. Geldart, Phys. Rev. B 7, 439 (1973).
[23]P. Jena and D. J. W. Geldart, Solid State Commun. 15, 139 (1974).
[24]M. B. Stearns and J. M. Norbeck, Phys. Rev. B 20, 3739 (1979).
[25]J. M. Norbeck and M. B. Stearns, J. Appl. Phys. 50, 2063 (1979).
[26]I. A. Campbell, J. Phys. C 2, 1338 (1969).
[27]R. E. Watson and L. H. Bennett, Phys. Rev. B 15, 502 (1977).
[28]Le Dang Khoi, P. Veillet, and I. A. Campbell, J. Phys. F 12, 2561 (1977).
[29]W. Leiper, J. D. Rush, M. F. Thomas, C. E. Johnson, F. W. D. Woodhams, C. Blaauw, and G. R. MacKay, J. Phys. F 7, 533 (1977).