Atomic Disorder in Heusler Co_2MnGe Measured by Anomalous Diffraction

B. Ravel,[1] J. O. Cross,[2] M. P. Raphael,[1] R. Ramesh,[3] V. Saraf,[3] V. G. Harris[1]
[1]Naval Research Laboratory, Washington, DC, U.S.A.
[2]University of Washington, Seattle, WA, U.S.A.
[3]University of Maryland, College Park, MD, U.S.A.

Introduction

The band theory predicts that full-Heusler material is a half-metallic ferromagnet (i.e., a material for which the conduction electrons are entirely spin polarized) [1, 2]. To date, however, this and similar Heusler materials have proven disappointing, displaying spin polarization values only slightly higher than those of metallic cobalt or iron [3]. The band theory further predicts that the conduction gap between the majority and minority spin states can be closed by the introduction of disorder into the crystal lattice [4]. Specifically, it predicts that anti-site disorder (at a level of a few percent) of the Mn sites being occupied by Co atoms is sufficient to close the gap. In neutron diffraction experiments [5] on a stoichiometrically correct, bulk isomorph, about 15% of Mn sites were found to be occupied by Co. Correspondingly, about 7.5% of the Co sites were occupied by Mn. The same sample had a spin polarization [6] of about 55%. We presume that the measured anti-site disorder explains the diminished spin polarization.

Measurement of anti-site disorder in thin films is more challenging. Neutron diffraction is impractical because of the small diffracting volume of a thin film. Laboratory x-ray diffraction is not fruitful because of the nearly identical scattering factors of Co and Mn at the Cu Kα energy. In this work, we present a synchrotron-based anomalous x-ray diffraction measurement that is well suited to thin films and directly measures the Co occupancy in the Mn sublattice in a thin film with precision comparable to the neutron diffraction measurement on bulk samples.

Methods and Materials

A film of Co_2MnGe was grown by pulsed-laser deposition (PLD) on a (100) GaAs substrate. By diffraction, we found the film to be nearly pure phase and highly textured along the growth direction. The film was about 700-Å thick, as measured by reflectivity. The sample was found by induction coupled plasma optical emission spectroscopy to be manganese-deficient. The actual stoichiometry was $Co_{2.16}Mn_{0.88}Ge_{1.00}$, with uncertainties of 0.02 for each element.

Our anomalous diffraction experiment at beamline 20-ID-C measures the energy dependence of a Bragg reflection as the incident photon energy is scanned through the K-shell absorption energy of the cobalt atom. The sample is mounted on a goniometer, and the θ and 2θ angles are adjusted to meet the Bragg condition at each energy. For this experiment, we measured a <111> reflection by 1-eV steps in the energy range of 7509-7909 eV, across the Co K edge at 7709 eV, where anomalous corrections [7] to the Co scattering amplitude change rapidly.

At each energy, we moved the detector to the calculated Bragg angle 2θ and measured the sample rocking curve $I(\theta)$. A set of these rocking curves across the measured energy range is shown in Fig. 1. Background scattering, including the jump in background fluorescence across the absorption edge, was removed by fitting each rocking curve as the sum of a Lorentzian and a line. The IFEFFIT program [8] was used for these fits.

A <111> reflection was chosen because it is particularly sensitive to the presence of Co in the Mn sublattice. Co_2MnGe crystallizes in the full-Heusler, C_21 structure, with space group $FM\bar{3}M$ and with Co, Mn, and Ge atoms at (¼,¼,¼), (0,0,0), and (½,½,½), respectively. At a <111> reflection, the structure factors for the Mn and Ge sublattices are nonzero but oppositely signed, while the structure factor for the Co sublattice is strictly 0. Despite its rapid variation in that energy range, the Co anomalous scattering correction will not contribute

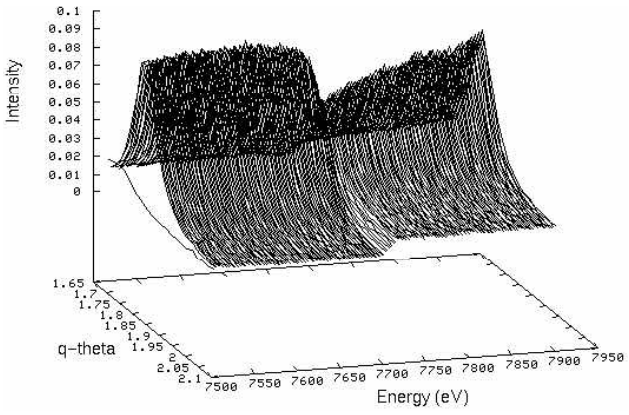

FIG. 1. Surface plot of a set of rocking curves about the <111> peak. At each energy between 7509 and 7909 eV, a rocking curve in q was measured.

to a <111> reflection unless Co atoms reside in lattice positions other than the sublattice nominally occupied by Co. In that case, the dependence of the diffracted intensity on the Co anomalous scattering will be evident and proportional to the amount of Co on the Mn sublattice.

Results

The diffracted intensity at each energy was found by performing fits like that shown in Fig. 2. The dotted line in Fig. 3 shows the energy dependence of the diffracted intensity. In this spectrum, we see the characteristic cusp of an anomalous diffraction scan followed by the diffraction anomalous fine structure (DAFS) [9]. We used IFEFFIT [8] to fit these data to the equation describing the energy and momentum-transfer dependence of the diffracted intensity, shown in Eq. (1):

$$I(\mathbf{q},E) = \alpha \left| \sum_n \left[f_{0,n}(\mathbf{q}) + f_n'(E) + i\, f_n''(E) \right] e^{i\mathbf{q}\cdot\mathbf{r}_n} \right|^2 \times A(\mathbf{q},E) L(\mathbf{q},E) + I_0(E). \quad (1)$$

In this equation, f_0 = the tabulated value [10] of the Thompson scattering for this momentum transfer, and f' and f'' are the anomalous corrections to the scattering factors. For Mn and Ge, tabulated values [7] are used. For Co, a fluorescence expanded x-ray absorption fine structure (EXAFS) spectrum taken on this sample was converted to f'' by the optical theorem [11], and f' was obtained by a Kramers-Krönig transform. $L(\mathbf{q},E)$ = the energy-dependent Lorentz correction $1/(E^3 \sin 2\theta)$. $A(\mathbf{q},E)$ = the absorption correction, a significant term in this energy range. Finally, α and $I_0(E)$ are empirical scaling and offset terms determined by fitting to the data.

Our fits used four floating parameters: α, the amplitude factor in Eq. (1); both the slope and the intercept of the $I_0(E)$ line; and the amount x of Co found on the Mn sublattice. Thus, in the summation in Eq. (1), each site in the Mn sublattice is occupied by x Co atoms and by $(1 - x)$ Mn atoms. The result of the fit is shown by the solid line in Fig. 3. The value of x found for this fit was 0.141 ±0.003, indicating that about 14% of the Mn sites are occupied by Co.

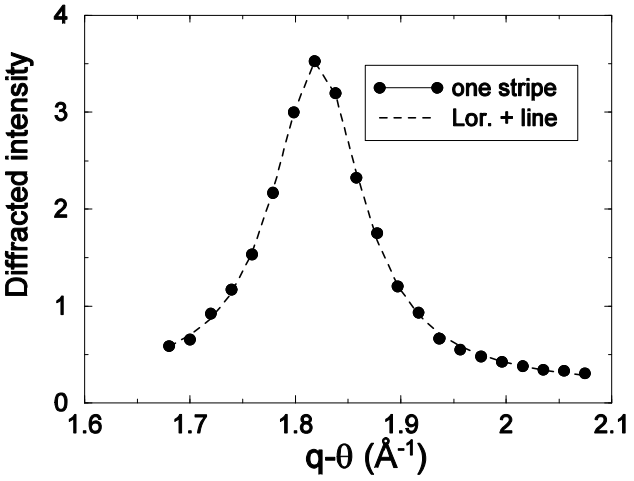

FIG. 2. A rocking curve about the <111> reflection (·) at one energy, plotted as a function of wave number. This curve is fit with a line plus a Lorentzian to the q rocking curve (dashed line).

Discussion

This anomalous diffraction technique is a precise way of measuring the content of Co on the Mn sublattice in a thin film sample. We found that in our sample, 14.1 ±0.3% of the Mn sublattice sites are occupied by Co. As stated above, this film is not a stoichiometric Heusler; there is excess Co, and Mn is deficient. This deviation from stoichiometry is consistent with the measured amount of Co on the Mn sublattice. This result is relevant because of the fact that the measurement and its analysis are independent of the reason for the presence of Co on the Mn sublattice. Band structure theory [4] suggests that anti-site disorder is a dominant reason for diminished spin polarization in Heusler materials. The technique presented here can accurately and precisely measure that disorder in Co_2MnGe.

Significant materials preparation issues remain to be resolved. We need to better understand how to grow stoichiometrically correct and pure-phase Heusler films, by either PLD or other methods. Then we need to identify growth conditions for correct, pure-phase materials that correlate to differing values of spin polarization. If these materials problems can be solved, the anomalous diffraction technique presented in this work can be used to correlate levels of spin polarization with anti-site disorder.

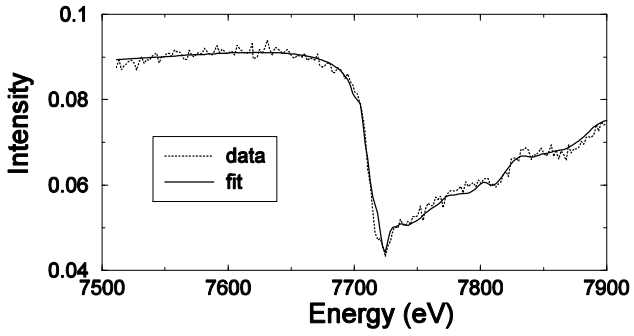

FIG. 3. The energy dependence of the <111> diffracted intensity (dotted line) and the best fit (solid line) to these data by using Eq. (1).

Acknowledgments

We thank the Pacific Northwest Consortium Collaborative Access Team (PNC-CAT) staff for their support. This work was supported in part by the American Society for Engineering Education. Use of the APS was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

References

[1] K. Ohta and H. Ishida, Appl. Spectrosc. **42**(6), 952 (1988).

[2] S. Ishida, T. Masaki, S. Fujii, and S. Asano, Physica B **245**, 1 (1998).

[3] S. F. Cheng, B. Nadgorny, E. E. Carpenter, K. M. Bussman, B. N. Das, and V. G. Harris, IEEE Trans. Magn. **37**, 2176 (2001).

[4] D. Orgassa, H. Fujiwara, T. C. Schulthess, and W. H. Butler, Phys. Rev. B **60**(19), 13237 (1999).

[5] B. Ravel, M. Raphael, V. Harris, and Q. Huang, Phys. Rev. B (in press, 2002).

[6] M. Raphael, B. Ravel, M. Willard, S. Cheng, B. Das, R. Stroud, K. Bussmann, J. Claassen, and V. Harris, Appl. Phys. Lett. **79**(26), 4396 (2001).

[7] D. T. Cromer and D. Liberman, J. Chem. Phys. **53**, 1891 (1970).

[8] M. Newville, J. Synchrotron Rad. **8**, 322 (2001).

[9] L. Sorensen, J. Cross, M. Newville, B. Ravel, J. Rehr, H. Stragier, C. Bouldin, and J. Woicik, in *Resonant Anomalous X-ray Scattering: Theory and Applications*, edited by G. Materlik, C. Sparks, and K. Fischer (North Holland, Amsterdam, The Netherlands, 1994).

[10] *International Tables for Crystallograpyhy*, edited by A. J. C. Wilson, Vol. C, Chap. 6, Table 6.1.1.4 (Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992).

[11] B. Cullity, *Elements of X-ray Diffraction*, 2nd ed. (Addison-Wesley, New York, NY, 1978).