Ferromagnetic resonance study of icosahedral and amorphous $Al_{55}Mn_{20}Si_{25}$ alloys

Sushil K. Misra and Lucjan E. Misiak*
Department of Physics, Concordia University, 1455 de Maisonneuve Boulevard West, Montreal, Quebec, Canada H3G 1M8

Dhirendra Bahadur
Advanced Centre for Materials Science, Indian Institute of Technology, Kanpur 208016, India

V. Srinivas and R. A. Dunlap
Department of Physics, Dalhousie University, Halifax, Nova Scotia, Canada B3H 3J5
(Received 26 May 1989)

Ferromagnetic resonance (FMR) studies of icosahedral and amorphous $Al_{55}Mn_{20}Si_{25}$ alloys are presented; the results suggest that Mn exists in more than one type of magnetic environment. In addition, the FMR signal is due to magnetic ordering. The temperature dependence of the magnetizations, as determined from the FMR measurements, indicates that the magnetic interactions in these alloys cannot be described entirely satisfactorily in terms of simple spin-wave theories.

I. INTRODUCTION

Since the first report of icosahedral symmetry in rapidly quenched aluminum transition-metal alloys by Shechtman *et al.*,[1] there has been considerable work measuring the structural, electrical, and magnetic properties of these and related quasicrystalline materials. While there has been controversy concerning the actual structure of these materials,[2–4] the general consensus seems to be that these structures are intermediate to crystalline and amorphous materials in the sense that they display long-range orientational ordering, but no translational order. While the magnetic properties of ferromagnetic crystalline and amorphous alloys have been studied for many years, a quasicrystalline material which exhibited ferromagnetic order was, until recently, unknown. Previous quasicrystalline alloys have exhibited, at most, relatively weak paramagnetism,[5] or in a few cases, spin-glass behavior at low temperatures.[6] Thus, although a number of theoretical predictions have been made concerning the effects of icosahedral order on magnetism,[7–9] experimental measurements of these properties have not been available. Recently, Dunlap *et al.*[10] have reported the existence of a ferromagnetic phase below about 120 K in some high Si content Al-Mn-Si quasicrystals. The availability of these materials allows for the study of the effects of icosahedral order on a variety of magnetic properties. The purpose of the present paper is to report *X*-band electron paramagnetic resonance (EPR) studies of both the icosahedral and amorphous $Al_{55}Mn_{20}Si_{25}$ alloys, along with a comparison of these results, with the previous magnetization studies on these alloys.[10]

II. EXPERIMENTAL METHODS

A sample of amorphous $Al_{55}Mn_{20}Si_{25}$ was prepared by arc melting high-purity elemental components under an argon atmosphere. These alloys were rapidly quenched from melt onto a single Cu roller with a surface velocity of $\sim 60\ m\,s^{-1}$. X-ray diffraction measurements showed that the resulting ribbons were fully amorphous.

A single-phase sample exhibiting quasicrystalline order with icosahedral symmetry was prepared by precipitating this phase from the amorphous structure by annealing according to the method of Dunlap *et al.*[10] Superconducting quantum interference device (SQUID) measurements revealed a Curie transition temperature of about 120 K.[10]

Conventional *X*-band (~ 9.4 GHz) electron paramagnetic resonance studies were carried out using a Varian V4502 spectrometer. Magnetic fields up to 600 mT were provided by a Varian Associates 12-inch electromagnet, powered by a Bruker power supply (B-MN50/200) and driven by a Bruker field controller (B-H15). The sample was placed in a TE_{102} cavity, and a modulation frequency of 400 Hz was used, except for the measurement displayed in Fig. 1, for which it was 100 kHz. Samples were prepared by sandwiching many layers of the as-quenched, or annealed ribbon, between pieces of tape. The measurements were made with the external magnetic field applied in the plane of the ribbons. The experimental electron paramagnetic resonance technique dealing with the measurements below the Curie transition temperature is referred to as ferromagnetic resonance (FMR). (In the following the terms FMR and EPR will be used interchangeably.)

III. RESULTS AND DISCUSSION

A. General features of the FMR spectra

Typical FMR spectra obtained at liquid-nitrogen temperature (79.5 K) and at room temperature are illustrated in Fig. 1 for the icosahedral (*i* phase) sample and the amorphous (*a* phase) sample of $Al_{55}Mn_{20}Si_{25}$.

The room-temperature (RT) EPR spectrum of the *a*-phase sample showed a weak and a broad line between 270 and 330 mT. The effective *g* factor associated with this resonance was determined to be ~ 2.21. At liquid-nitrogen temperature (LNT) this line was found to de-

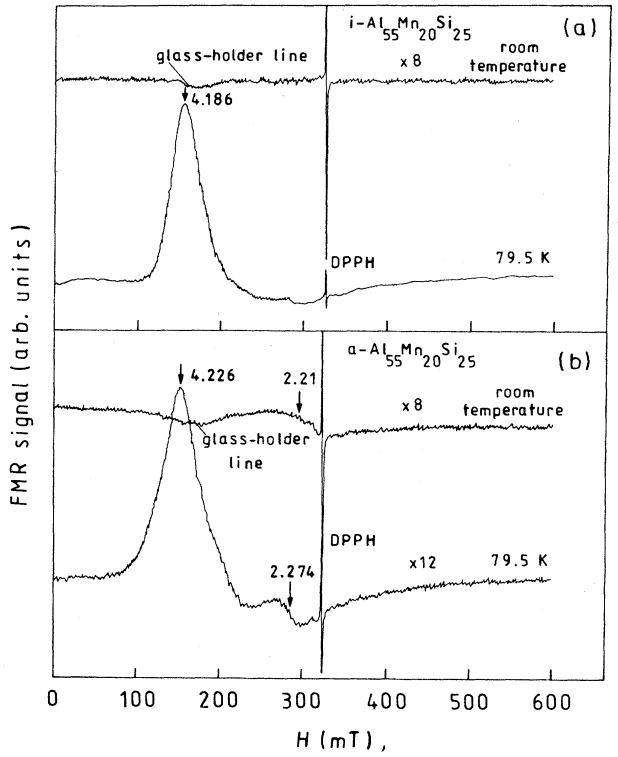

FIG. 1. First-derivative X-band FMR spectra of (a) icosahedral $Al_{55}Mn_{20}Si_{25}$ and (b) amorphous $Al_{55}Mn_{20}Si_{25}$, recorded at room temperature and at liquid-nitrogen temperature (79.5 K). The "glass holder line" in the figure indicates the signal due to the sample holder. The corresponding g factors are given for the various resonances. Note the different scale factors associated with different spectra, due to the difference in the presence of Mn centers.

crease in width by about a factor of 2, and to shift to somewhat lower fields; giving an effective g factor of 2.274. The LNT spectrum, however, was dominated by the presence of a new line near 150 mT. This resonance gives an effective g factor of 4.226.

The RT spectrum of the i-phase sample did not exhibit any measurable resonances. The LNT spectrum of the i-phase sample showed the appearance of two resonance lines—a very weak line near 285 mT, giving an effective g factor of ~ 2.27 and a very strong line near 155 mT, giving an effective g factor of 4.186.

The above observation for both the amorphous and icosahedral phases suggests the duality of Mn sites in the alloys.[11–13] As discussed below, the larger peak observed in the two samples at LNT appears below the magnetic-ordering temperature; both its intensity and position are highly dependent on temperature. It is, therefore, reasonable to associate this resonance with magnetically ordered Mn. The weaker resonance which appears, at least in the amorphous sample, above the Curie temperature shows a relatively weak temperature dependence, and is presumably due to paramagnetic Mn. This distinction between magnetically ordered Mn and paramagnetic Mn has been previously made on the basis of magnetization measurements in these alloys.[10]

It is noteworthy that the $g \sim 4.2$ resonance observed at LNT in the i-phase sample, is about 10 times more intense than the same resonance in the a-phase sample. As well, it is observed that this resonance is narrower in the i-phase sample than in the a-phase sample. Normally, the linewidth contributions in ferromagnetic samples come from porosity, surface pins, eddy currents, anisotropy, and inhomogeneous demagnetization.[14] Since no surface treatments were given to the samples, the contribution due to surface pins should be the same in both the a- and i-phase samples. The contribution due to porosity and eddy currents should also remain essentially the same. As the icosahedral phase is more ordered than its amorphous counterpart,[15] short-range structural inhomogenetics in the amorphous phase are presumably responsible for the increase in the linewidth.[14]

As for the paramagnetic $g \sim 2.27$ resonance at LNT, its integrated intensity is about 0.1% in the i-phase sample, whereas it is about 4.5% in the a-phase sample. Such amounts of paramagnetic Mn are either much below the limit, or about the limit (3–4 %), that can be detected by x-ray measurements to determine unequivocally whether these paramagnetic Mn spins belong to another phase.

The high-field resonance in the a-phase sample is narrower and more intense at 79.5 K than that at room temperature. The observed change in linewidth can be ascribed to spin-lattice relaxation. The increase in intensity with decrease in temperature obviously arises due to an increased Boltzmann population difference between the two energy levels, participating in resonance.[16]

B. Temperature variations of the FMR line intensity and the g factor

The integrated intensity of the FMR line, $\mathcal{I}$, is represented by the area under the first-derivative FMR absorption line. $\mathcal{I}$ is a measure of the spin-only susceptibility: $\mathcal{I} = K I_m \Delta H_{1/2}^2$, where I_m is the peak height, $\Delta H_{1/2}$ is the full width at half maximum, and K is a constant. The dependence of $\mathcal{I}$ on temperature for the two samples presently studied is illustrated in Fig. 2. The data are plotted only up to 123 K, above which the intensity was too low to be determined. The relative magnitudes of $\mathcal{I}$ for the icosahedral and amorphous samples are consistent with the relative values of the saturation magnetizations reported by Dunlap *et al.*[10] The upturn in $\mathcal{I}$ at low temperatures for the i-phase sample is consistent with that observed previously by SQUID magnetization measurements of this sample.[10] Although Dunlap *et al.*[10] have suggested, but have been unable to substantiate from their magnetization measurements, that this is due to that fraction of the Mn spins which have not undergone ferromagnetic ordering, the present result based on the magnetization deduced from the FMR line intensity suggests that the upturn at low temperatures is due to the ferromagnetic phase alone.

The temperature dependences of the effective isotropic g values in the two, a- and i-phase samples, are similar, as illustrated in Fig. 3, except at very low temperatures

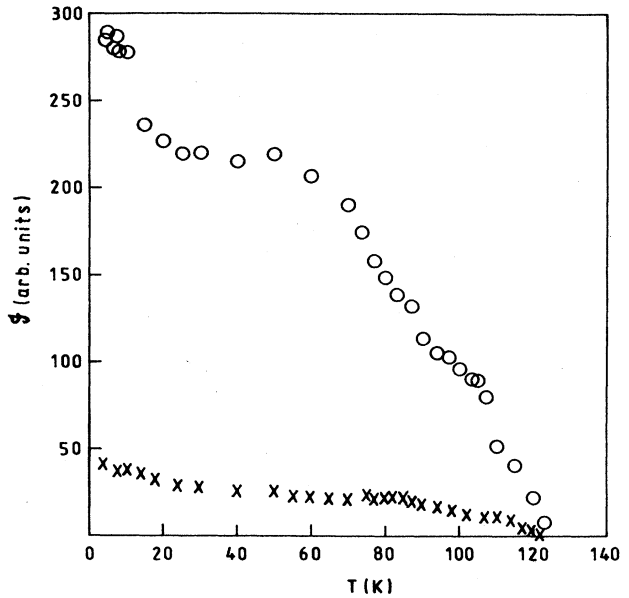

FIG. 2. The integrated intensity, $\mathcal{I}$ ($\propto I_m \Delta H_{1/2}^2$, where I_m is the amplitude and $\Delta H_{1/2}$ is the full width at half maximum), of the major FMR line as a function of temperature (T) for amorphous (×) and icosahedral (○) phases of $Al_{55}Mn_{20}Si_{25}$ alloys.

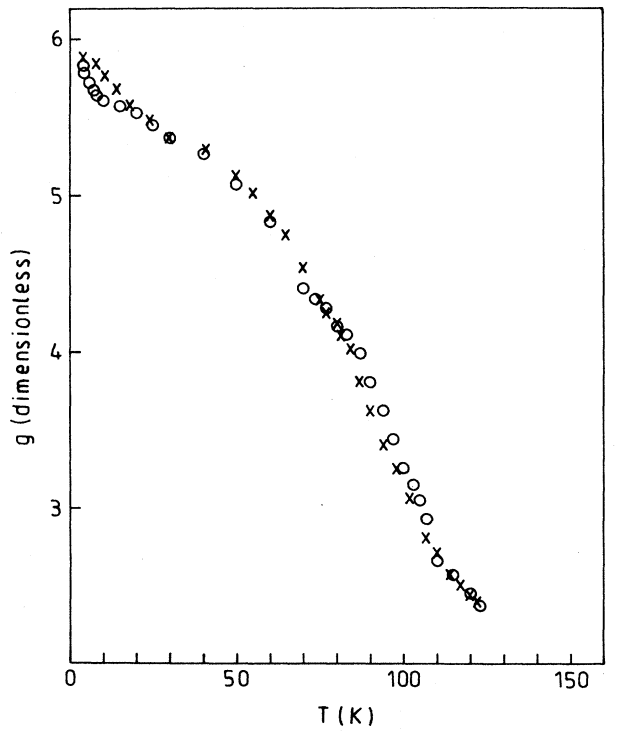

FIG. 3. Temperature dependence of the effective g factor in ferromagnetic range for amorphous (×) and icosahedral (○) $Al_{55}Mn_{20}Si_{25}$ alloys.

(4.2–20 K), where the i-phase sample exhibits the well-defined upturn seen in $\mathcal{I}$ and M. A noteworthy feature in this figure is a large variation in the g values as a function of temperature. The effective g values vary between 2.4 and 5.9, as the temperature rises from 4.2 to 123 K due to the temperature-dependent magnetization[17] in the ferromagnetic phase.

C. Magnetization

The magnetization of the ferromagnetic samples can be determined from the FMR measurements using the expression[18]

$$(\omega/\gamma)^2=(H_a+H_{\rm an}-H_{\rm dem})(H_a+H'_{\rm an}-H_{\rm dem}+4\pi M)\ , \tag{1}$$

where H_a is the applied external field, ω is the angular frequency of microwave radiation, γ is the gyromagnetic ratio, and $H_{\rm dem}$ is the static demagnetizing field, which is negligible (~0.2 mT when the applied magnetic field is in the sample plane). $H_{\rm an}$ and $H'_{\rm an}$ represent any anisotropy fields that may be present, which can be assumed to be $H_{\rm an}=H'_{\rm an}\approx 0$.[18] The magnetization (M) is, therefore, given by the equation

$$M=\frac{1}{4\pi}\left[\left(\frac{h\nu}{g\mu_B}\right)^2\frac{1}{H_a}-H_a\right]\ , \tag{2}$$

where ν is the klystron frequency (~9.4 GHz), μ_B is the Bohr magneton, and the g factor is assumed to be constant below the Curie temperature for both the samples. In the present work $g=2.3$ has been used, which is the effective g value at the temperature above T_c (Fig. 3) where the line intensity is approximately zero.

In order to consider the possibility that there exist spin waves resulting from long-wavelength magnetic excitations in these ferromagnets, the expression[19,20]

$$M(T)=M_0(1-BT^{3/2}-CT^{5/2})\ , \tag{3}$$

where M_0, B, and C are the constants, was used to least-squares fit the experimental magnetization values, as estimated from the FMR data, using Eq. (2), for both the amorphous and icosahedral alloys in the temperature range 4.2–123 K. The values of the constants of Eq. (3), as obtained from these fits, are listed in Table I, and the magnetization $M(T)$ is plotted as a function of $T^{3/2}$ in Figs. 4(a) and 4(b) for the amorphous and icosahedral Al-Mn-Si samples, respectively. The dependence of the magnetization on temperature follows the same general trend as in the case of conventional amorphous ferromag-

TABLE I. Parameters describing the magnetization as function of temperature, obtained from a least-squares fitting of the FMR data to Eq. (3) (a denotes amorphous, i denotes icosahedral).

Alloy	$4\pi M_0$ (kOe)	B ($K^{-3/2}$)	C ($K^{-5/2}$)
a-$Al_{55}Mn_{20}Si_{25}$	6.60	7.0×10^{-4}	1.4×10^{-7}
i-$Al_{55}Mn_{20}Si_{25}$	6.35	6.7×10^{-4}	1.6×10^{-7}

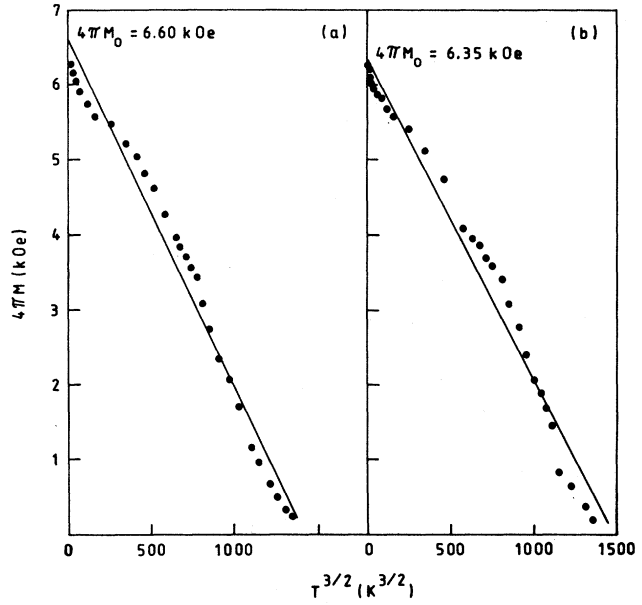

FIG. 4. Temperature ($T^{3/2}$) dependence of the magnetization for (a) amorphous and (b) icosahedral $Al_{55}Mn_{20}Si_{25}$ alloys.

nets.[18] However, as seen from Figs. 4(a) and 4(b) there are significant deviations from the $T^{3/2}$ behavior in both cases. Again, as noted in Sec. III B above, the rise of magnetization at low temperatures, as deduced from the FMR line position is due to the ferromagnetic phase alone. Thus, the problem with the $T^{3/2}$ law is not due to two ferromagnetic and paramagnetic phases in the sample but rather due to one, i.e., the ferromagnetic phase only.

The relative values of B and C from Table I can be used to estimate the mean range of exchange interactions, $\langle r \rangle$, in these materials. This range is written as[18,20]

$$\langle r \rangle = \left[\frac{16}{3k_B} \frac{\zeta(\frac{3}{2})}{\zeta(\frac{5}{2})} \frac{C}{B} D \right]^{1/2}, \quad (4)$$

where D is the spin-wave stiffness, which is given as

$$D = \frac{k_B}{4\pi} \left[\zeta(\tfrac{3}{2}) \frac{g\mu_B}{M_0 B} \right]^{2/3}. \quad (5)$$

In Eqs. (4) and (5), $\zeta(i)$ is the Riemann zeta function and k_B is the Boltzmann constant. The above equations yield values of $\langle r \rangle \sim 0.8$ Å for both the phases of $Al_{55}Mn_{20}Si_{25}$ investigated presently. The observed average Mn-Mn neighbor distance, i.e., the ferromagnetic order, is about 4.5 Å in these alloys;[21] it indicates that the present estimate of $\langle r \rangle$ is clearly inconsistent with the observed ferromagnetic order. Although the values of $\langle r \rangle$ as determined using Eqs. (4) and (5) represent only rough estimates, they are not entirely consistent with the spin-wave theory in these alloys; this is also concluded from the deviations from the $T^{3/2}$ behavior, predicted by the spin-wave theory, as seen in Figs. 4(a) and 4(b).

IV. CONCLUDING REMARKS

The present FMR measurements reveal that icosahedral amorphous $Al_{55}Mn_{20}Si_{25}$ alloys exhibit a sizable FMR signal at low temperatures. This observation is in contrast to that found in paramagnetic Al-Cr-Mn-Si quasicrystals,[22] where the FMR signal is absent at all temperatures, indicating that the FMR signal may be associated with the presence of magnetic ordering.[13] The disappearance of the major FMR signal in the $Al_{55}Mn_{20}Si_{25}$ alloys is consistent with the values of T_c determined on the basis of SQUID magnetization studies.[10]

The present studies on icosahedral and amorphous Al-Mn-Si alloys indicate that the magnetic properties of the two phases are very similar. The anomalous values of the mean exchange-interaction range obtained presently, in contrast to Fe-based ferromagnetic amorphous alloys,[18] suggests that these materials cannot be described entirely in the context of conventional spin-wave theories of ferromagnetization. Similar anomalous behavior is observed in ferromagnetic Al-Mn-Si and Al-Mn-Ge quasicrystals on the basis of the low ratio of ferromagnetic Mn moment to Curie temperature.[10,23] Dunlap and coworkers[10,24,25] have suggested that the anomalous magnetic behavior in these materials may be the result of weak itinerant ferromagnetism, or a noncollinear spin arrangement. As well, the present measurements add validity to the suggestion of the presence of more than one distinct Mn site environment,[12] that these different sites display different magnetic behaviors,[13] and that this site duality is also present in the ferromagnetic state.

The upturn in magnetization at low temperatures, and the problem of magnetization with the $T^{3/2}$ law, is not due to two magnetic phases in the sample but due solely to the ferromagnetic phase, as deduced presently from the FMR line position and the FMR line intensity.

ACKNOWLEDGMENTS

We are grateful to the Natural Sciences and Engineering Research Council of Canada for partial financial support (Grant No. A4485-SKM and Grant No. CRD-8715-RAD). One of us (D.B.) is thankful to the Department of Science and Technology, Government of India for support.

*Permanent address: Department of Experimental Physics, Maria Curie-Skłodowska University, Place M. Curie-Skłodowskiej 1, 20-031 Lublin, Poland.

[1]D. Shechtman, I. Blech, D. Gratias, and J. W. Cahn, Phys. Rev. Lett. **53**, 1951 (1984).
[2]L. Pauling, Phys. Rev. Lett. **58**, 365 (1987).
[3]J. W. Cahn, D. Shechtman, and D. Gratias, J. Mater. Res. **1**, 13 (1986).

[4]H. B. Elswijk, P. M. Bronsveld, and J. Th. M. De Hosson, Phys. Rev. B **37**, 4261 (1988).
[5]J. J. Hauser, H. S. Chen, and J. V. Waszczak, Phys. Rev. B **33**, 3577 (1986).
[6]M. E. McHenry, R. A. Dunlap, R. Chatterjee, A. Chow, and R. C. O'Handley, J. Appl. Phys. **63**, 4255 (1988).
[7]M. E. McHenry, M. E. Eberhart, R. C. O'Handley, and K. H. Johnson, Phys. Rev. Lett. **56**, 81 (1986).
[8]M. E. McHenry and R. C. O'Handley, in *Science and Technology of Rapidly Quenched Alloys,* Vol. 80 of *Materials Research Society Symposium Proceedings,* edited by M. Tenhover, W. L. Johnson, and L. E. Tanner (MRS, Pittsburgh, 1987), p. 363.
[9]M. E. McHenry and R. C. O'Handley, Mater. Sci. Eng. **99**, 377 (1988).
[10]R. A. Dunlap, M. E. McHenry, V. Srinivas, D. Bahadur, and R. C. O'Handley, Phys. Rev. B **39**, 4808 (1989).
[11]R. A. Dunlap, D. W. Lawther, and D. J. Lloyd, Phys. Rev. B **38**, 3649 (1988).
[12]M. Eibschutz, M. E. Lines, H. S. Chen, J. V. Waszczak, G. Papaefthymiou, and R. B. Frankel, Phys. Rev. Lett. **59**, 2443 (1987).
[13]M. E. McHenry, V. Srinivas, D. Bahadur, R. C. O'Handley, D. J. Lloyd, and R. A. Dunlap, Phys. Rev. B **39**, 3611 (1989).
[14]D. Bahadur, R. Bilas, P. Chand, and R. A. Dunlap, J. Mater. Sci. **22**, 2477 (1987).
[15]R. A. Dunlap, D. W. Lawther, and R. H. March, J. Phys. F **17**, L39 (1987).
[16]A. K. Bandyopadhyay, J. Zarzycki, P. Auric, and J. Chappert, J. Non-Cryst. Solids **40**, 353 (1980).
[17]F. Mehran, K. W. H. Stevens, and F. Holtzberg, Phys. Rev. B **17**, 3707 (1978).
[18]S. M. Bhagat, M. L. Spano, and K. V. Rao, J. Appl. Phys. **50**, 1580 (1979).
[19]C. L. Chien and R. Hasegawa, Phys. Rev. B **16**, 2115 (1977).
[20]J. D. Axe, G. Shirane, T. Mizoguchi, and K. Yamauchi, Phys. Rev. B **15**, 2763 (1977).
[21]H. S. Chen, D. Koskenmaki, and C. H. Chen, Phys. Rev. B **35**, 3715 (1987).
[22]S. K. Misra, L. E. Misiak, D. Bahadur, V. Srinivas, and R. A. Dunlap (unpublished).
[23]A.-P. Tsai, A. Inoue, T. Masumoto, and N. Kataoka, Jpn. J. Appl. Phys. **27**, L2252 (1988).
[24]R. A. Dunlap and V. Srinivas, Phys. Rev B **40**, 704 (1989).
[25]R. A. Dunlap, M. E. McHenry, and R. C. O'Handley (unpublished).