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NEUTRON DIFFRACTION STUDY OF THE MAGNETIC STRUCTURES OF
 CeMn_2Ge_2 and CeMn_2Si_2

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ABSTRACT

The magnetic properties of the layered compounds of the form RMn_2X_2 (R=Rare Earth, X=Si, Ge) have been thought to be sensitive to the intralayer Mn-Mn distance. Thus it has been reported that the Mn moments in CeMn_2Si_2 are aligned antiferromagnetically (AF) below $T_N=380\text{K}$, while the Mn moments in CeMn_2Ge_2 are ferromagnetic (FM) below $T_C=316\text{K}$. Recently, however, there has been some debate about the actual magnetic structures of this family of compounds, and for this reason we have performed high-resolution neutron powder diffraction measurements on these compounds for temperatures between 12K and 550K. Our measurements indicate that at high temperatures both compounds are paramagnetic. Below $T_N=380\text{K}$ CeMn_2Si_2 becomes a collinear AF, with a structure similar to that reported by Siek et al. in which the magnetic propagation vector is $\tau=(0\ 0\ 1)$. CeMn_2Ge_2 , on the other hand, exhibits two different magnetic transitions. At $T_N\approx 415\text{K}$ there is a transition to a collinear AF phase characterized by the commensurate propagation wavevector $\tau=(1\ 0\ 1)$. At $T_C\approx 318\text{K}$ there is a transition to a conical structure with a ferromagnetic component along the c -axis and a helical component in the ab plane. The helical component is characterized by the incommensurate propagation vector $\tau=(1\ 0\ 1-q_z)$, where q_z is temperature dependent. These findings are consistent with the recent results of Welter et al.

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Introduction

The family of layered compounds of the form RM_2X_2 (R = Rare Earth, M = Transition metal, X = Si, Ge) crystallizes with the ThCr_2Si_2 ($I4/mmm$) structure and exhibits a rich variety of interesting physical phenomena that include superconductivity, magnetism, mixed valence, heavy fermion or Kondo behavior. Of particular interest is the system CeMn_2X_2 , which exhibits magnetic moments only at the Mn sites. In this system the Mn atoms form a simple tetragonal lattice and are coupled with an exchange interaction that seems to be sensitive to the Mn-Mn distances along the c -axis (interlayer exchange) and relatively insensitive to the Mn-Mn distances within the $(0\ 0\ 1)$ planes (intralayer exchange). It has been reported that the Mn moments in CeMn_2Si_2 are aligned ferromagnetically within the $(0\ 0\ 1)$ planes, and that these planes are coupled antiferromagnetically below $T_N=379\text{K}$.¹ The CeMn_2Ge_2 system, on the other hand, has been reported to be ferromagnetic (FM) below $T_C=316\text{K}$.^{2,3} Recently Venturini et al.⁴ have reported that in the related compounds LaMn_2Si_2 and LaMn_2Ge_2 there is strong evidence of dominant intralayer antiferromagnetic interactions, which give rise to conical incommensurate phases at low temperatures. These results suggest that the nature of the magnetic interactions in this family of compounds is more complex than originally thought, and that the magnetic structures of CeMn_2Si_2 and CeMn_2Ge_2 should be reexamined. For this reason we have performed high-resolution neutron powder diffraction measurements on these compounds to resolve the magnetic structures and the nature of the magnetic interactions in these systems. In this paper we report the findings of the preliminary analysis of the results of these measurements. We found that at high temperatures both compounds are paramagnetic. CeMn_2Si_2 becomes a collinear antiferromagnet below $T_N\approx 380\text{K}$, with a structure similar to that reported by Siek et al.,¹ in which the magnetic propagation vector is $\tau=(0\ 0\ 1)$. Below $T_N\approx 420\text{K}$ CeMn_2Ge_2 is a collinear antiferromagnet with a

commensurate propagation wavevector $\tau=(1\ 0\ 1)$. Below $T_C \approx 318\text{K}$ the Mn moments in this system exhibit a conical structure with a ferromagnetic component along the c -axis and a helical component in the ab plane, similar to that of LaMn_2Ge_2 reported for by Venturini et al.⁴ This helical component is characterized by the incommensurate propagation vector $\tau=(1\ 0\ 1-q_z)$, where q_z is temperature dependent and varies from 0 (at T_C) to 0.32 reciprocal lattice units (at $T=12\text{K}$). These findings are consistent with the recent results reported by Welter et al.⁵

Experimental

About 10g of CeMn_2Ge_2 and CeMn_2Si_2 were prepared by arc melting stoichiometric amounts of the constituents in an argon atmosphere. X-ray diffraction analysis showed that these specimens had no significant amounts of impurity phases. The samples were powdered and loaded in thin-walled aluminum or vanadium cells for the neutron diffraction measurements. For the measurements between 12K and 330K the cells were sealed in a He gas environment, and then placed in a closed cycle He refrigerator. For the high temperature measurements ($330\text{K} < T < 550\text{K}$) the cells were placed in a furnace. The neutron diffraction measurements were performed at the HB4 high-resolution powder diffractometer at the High Flux Isotope Reactor at Oak Ridge National Laboratory using neutron wavelengths of 1.417 Å and 2.222 Å.

CeMn_2Si_2

Powder diffraction patterns of CeMn_2Si_2 were collected between 12K and 430K. At 430K there was no evidence of any magnetic contribution to the diffraction pattern, and the crystal structure at this temperature was refined using the computer program RIETAN.⁶ The refined structural parameters are consistent with the published values for this material with the Ce, Mn and Si atoms at the $2(a)$, $4(d)$ and $4(e)$ sites of the space group

$I4/mmm$, $a=4.0417(6)\text{\AA}$, $c=10.5546(19)\text{\AA}$, and $z=0.382(1)$ (where z is the variable fractional coordinate of the Si atoms). In this space group the nuclear reflection conditions for $(h k l)$ are $h+k+l=2n$. An extra reflection condition, $l=2n$, exists for the scattering contribution from the Mn sites. As the temperature was lowered two superlattice peaks were observed. These could be indexed as the $(1\ 1\ 1)$ (see figure 1) and the $(1\ 1\ 3)$ reflections. These superlattice peaks appeared below $T_N \approx 380\text{K}$ and persisted all the way down to 12K . These findings are similar to those reported by Siek et al.¹ and correspond to an antiferromagnetic structure with a propagation vector $\tau=(0\ 0\ 1)$. The absence of reflections of the form $(0\ 0\ 2n\pm 1)$ indicates that the magnetic moments are parallel to the c -axis. In this collinear antiferromagnetic structure the magnetic moment M_z at the Mn site \mathbf{r}_1 is

$$M_z(\mathbf{r}_1)=M_0 \cos(\mathbf{r}_1 \cdot \boldsymbol{\tau}), \quad (1)$$

where $\boldsymbol{\tau}$ is the propagation vector characteristic of the magnetic structure in reciprocal lattice units, and M_0 is the magnitude of the magnetic moment. Thus in this structure all the Mn moments in the $(0\ 0\ 1)$ planes are coupled ferromagnetically, while the moments in adjacent $(0\ 0\ 1)$ planes are coupled antiferromagnetically. The magnetic moment per Mn atom at 12K was calculated from the intensities of the peaks shown in figure 1. In this calculation a small correction was made to account for the preferred orientation present in the powder. The calculated moment was of $1.9(2)\ \mu_B$ per Mn atom. This value is lower than the value $2.30(5)\ \mu_B$ reported by Siek et al.¹ and lower than the paramagnetic moment of $3.3\ \mu_B$ reported by Liang et al.⁷ At $T=12\text{K}$ the refined structural parameters were $a=3.9913(4)\text{\AA}$, $c=10.4935(13)\text{\AA}$, and $z=0.3805(8)$

CeMn₂Ge₂

Powder diffraction patterns of CeMn₂Ge₂ were collected between 12K and 550K. At 550K there was no evidence of any magnetic contribution to the diffraction pattern, and the crystal structure at this temperature was refined using the computer program RIETAN.⁶ This structure is similar to that of CeMn₂Si₂, with the Ce, Mn and Ge atoms at the 2(*a*), 4(*d*) and 4(*e*) sites of the space group *I4/mmm*, the refined structural parameters at 521K were $a=4.1623(3)\text{\AA}$, $c=11.0081(9)\text{\AA}$, and $z=0.3832(5)$ (where z is the variable fractional coordinate of the Ge atoms). As the temperature was lowered we found evidence of two magnetic transitions. Below $T_N\approx 415\text{K}$ the intensity of the (1 0 1) reflection increased, reaching a maximum at about $T=320\text{K}$ and then dropped rapidly to the same level of the high temperature patterns. Below $T_C\approx 315\text{K}$ magnetic satellites appeared in the vicinity of the (1 0 1) (see figure 2), (1 0 3), (1 0 5), (2 1 1) and (2 1 3) reflections, at the same time that the intensity of the (1 1 0), (1 1 2), (1 1 4) and (2 0 2) peaks increased. The intensities of the reflections (0 0 2n) remained unchanged in the whole temperature range studied. These observations are consistent with the existence of two different magnetic phases in CeMn₂Ge₂.

The enhancement of the (1 0 1) reflection below T_N could originate either by the appearance of ferromagnetic ordering of the Ce atoms, or by the appearance of antiferromagnetic ordering of the Mn atoms (i.e., by the formation of a superlattice of Mn atoms). The magnetic ordering of the Ce atoms, however, would also increase the intensity of most of the allowed nuclear reflections. This intensity enhancement has not been observed, indicating that no magnetic ordering is associated with the Ce atoms. This observation is consistent with earlier reports that Ce is nonmagnetic in this family of compounds.⁸⁻¹⁰ Other Lanthanides in RMn_2X_2 systems exhibit magnetic order but at much lower temperatures.⁸ The enhancement of the

(1 0 1) reflection can then be attributed to the antiferromagnetic ordering of the Mn atoms with a characteristic propagation wavevector $\tau=(1\ 0\ 1)$. As in the case of CeMn_2Si_2 the direction of the magnetic moments is parallel to the c -axis. Unlike the CeMn_2Si_2 system, however, both the intralayer and interlayer couplings of the Mn moments are antiferromagnetic, their directions given by equation (1).

The enhancement of the (1 1 0), (1 1 2), (1 1 4) and (2 0 2) peaks below $T_C \approx 315\text{K}$ can be attributed to the development of a ferromagnetic alignment of the Mn moments. The appearance of magnetic satellites at the same temperature can be attributed to the simultaneous appearance of a helical component of the Mn moments in the ab plane, with a characteristic wavevector $\tau=(1\ 0\ 1-q_z)$. The value of q_z is incommensurate with the lattice and is temperature dependent (see figure 3), varying from 0 (at T_C) to ≈ 0.32 (at 12K). In this structure the M_x, M_y , and M_z components of the magnetic moment $\mathbf{M}(\mathbf{r}_1)$ are given by:

$$\begin{aligned} M_x(\mathbf{r}_1) &= M_0 \cos(\mathbf{r}_1 \cdot \boldsymbol{\tau} + \phi), \\ M_y(\mathbf{r}_1) &= M_0 \sin(\mathbf{r}_1 \cdot \boldsymbol{\tau} + \phi), \\ M_z(\mathbf{r}_1) &= M_1. \end{aligned} \quad (2)$$

These components result in a conical structure similar to that described by Venturini et al. for LaMn_2Ge_2 .⁴ The refined ferromagnetic component M_z for Mn at $T=12\text{K}$ was $2.4(2)\mu_B$. The refined structural parameters at this temperature were $a=4.1291(2)\text{\AA}$, $c=10.9016(7)\text{\AA}$, and $z=0.3820(4)$

Discussion

The nature of the magnetic interactions in the systems under study is more complex than originally thought. The short distance between the Mn nearest neighbors ($a\sqrt{2}/2$) is suggestive of strong direct exchange interactions between the magnetic ions. The relatively large distance ($c/2$)

between the Mn (0 0 1) planes suggests indirect exchange interactions mediated by the Ge/Si and Ce atoms. For CeMn_2Si_2 the intralayer exchange interaction between Mn moments is ferromagnetic, while the interlayer is antiferromagnetic. For CeMn_2Ge_2 on the other hand, the intralayer exchange is antiferromagnetic, while the interlayer is such that gives rise to a transition from a commensurate antiferromagnetic phase to an incommensurate conical structure. The nature of this commensurate-to-incommensurate phase transition, which takes place with a magnetic moment reorientation is of special interest and should be studied further. Recent bulk magnetization measurements on a specimen of CeMn_2Ge_2 (from the same batch as our sample) revealed an anomaly in the magnetization at the same temperature where this spin reorientation takes place.¹⁰ When this work was in progress we learned of the recent published results of Welter et al.⁵ on CeMn_2Ge_2 ; our results on this system are in general agreement with theirs. Our results are also in general agreement with the recent Mössbauer experiments by Nowick et al.¹¹

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FIGURE CAPTIONS

Figure 1. Partial neutron powder diffraction pattern for CeMn_2Si_2 at $T=410\text{K}$ and 12K . The low temperature $(1\ 1\ 1)$ peak is of magnetic origin and is indicative of an antiferromagnetic structure with a characteristic propagation wavevector $\tau=(0\ 0\ 1)$ (see text). The solid lines are the result of fits to Gaussian lineshapes. The peak labeled with a question mark corresponds to an unidentified impurity phase. The neutron wavelength for this measurement was $\lambda=2.22\text{\AA}$.

Figure 2. Partial neutron powder diffraction pattern for CeMn_2Ge_2 at $T=521\text{K}$ and 12K . The low temperature magnetic satellites in the vicinity of the $(1\ 0\ 1)$ peak are of magnetic origin and are indicative of a helical component of the Mn Magnetic moments with characteristic propagation wavevector $\tau=(1\ 0\ 1-q_z)$ (see text). The neutron wavelength for this measurement was $\lambda=2.22\text{\AA}$.

Figure 3. Temperature dependence of q_z for CeMn_2Ge_2 . In this figure q_z is given in reciprocal lattice units (r. l. u).

CeMn₂Si₂

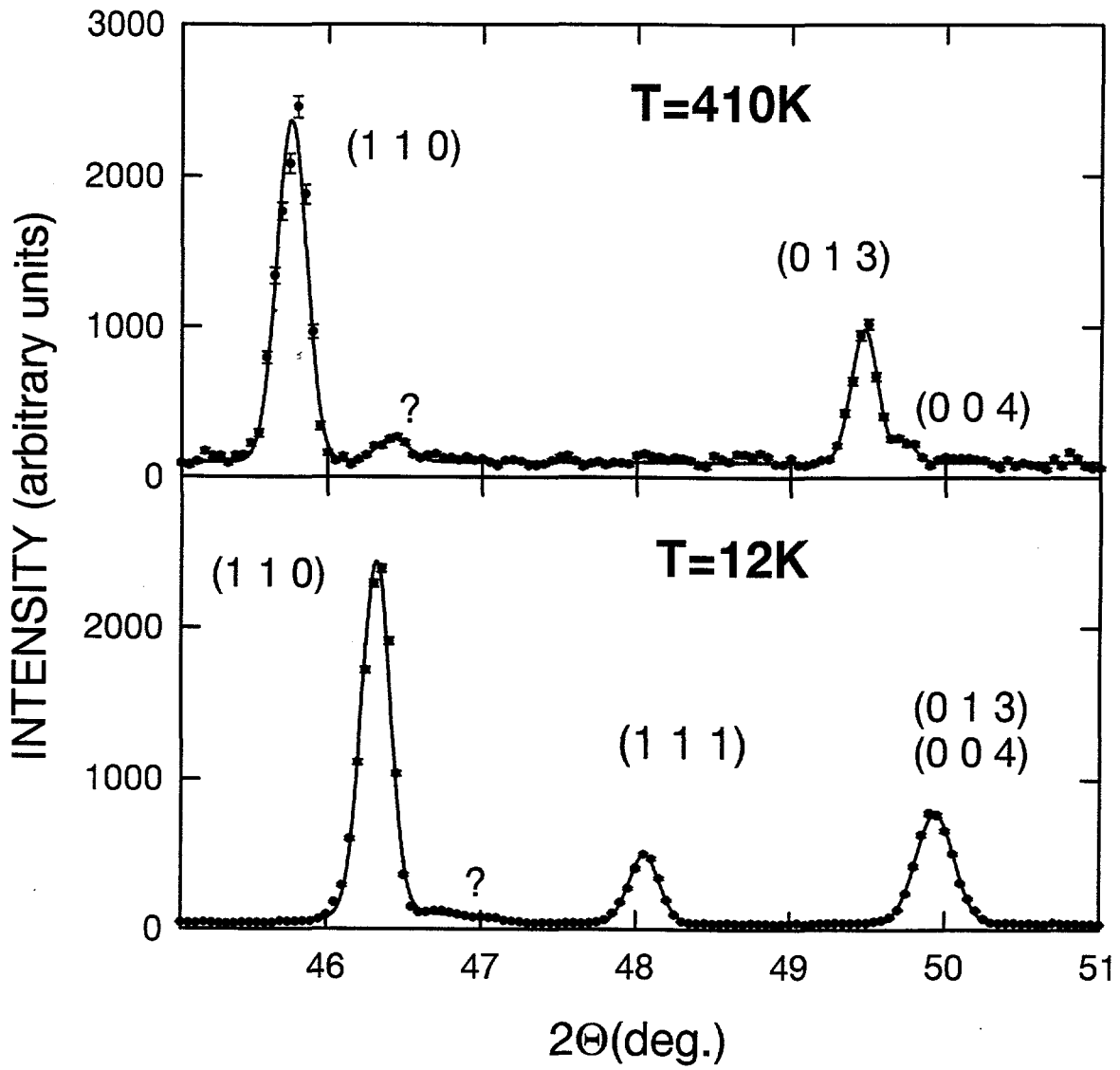


Figure 1

CeMn₂Ge₂

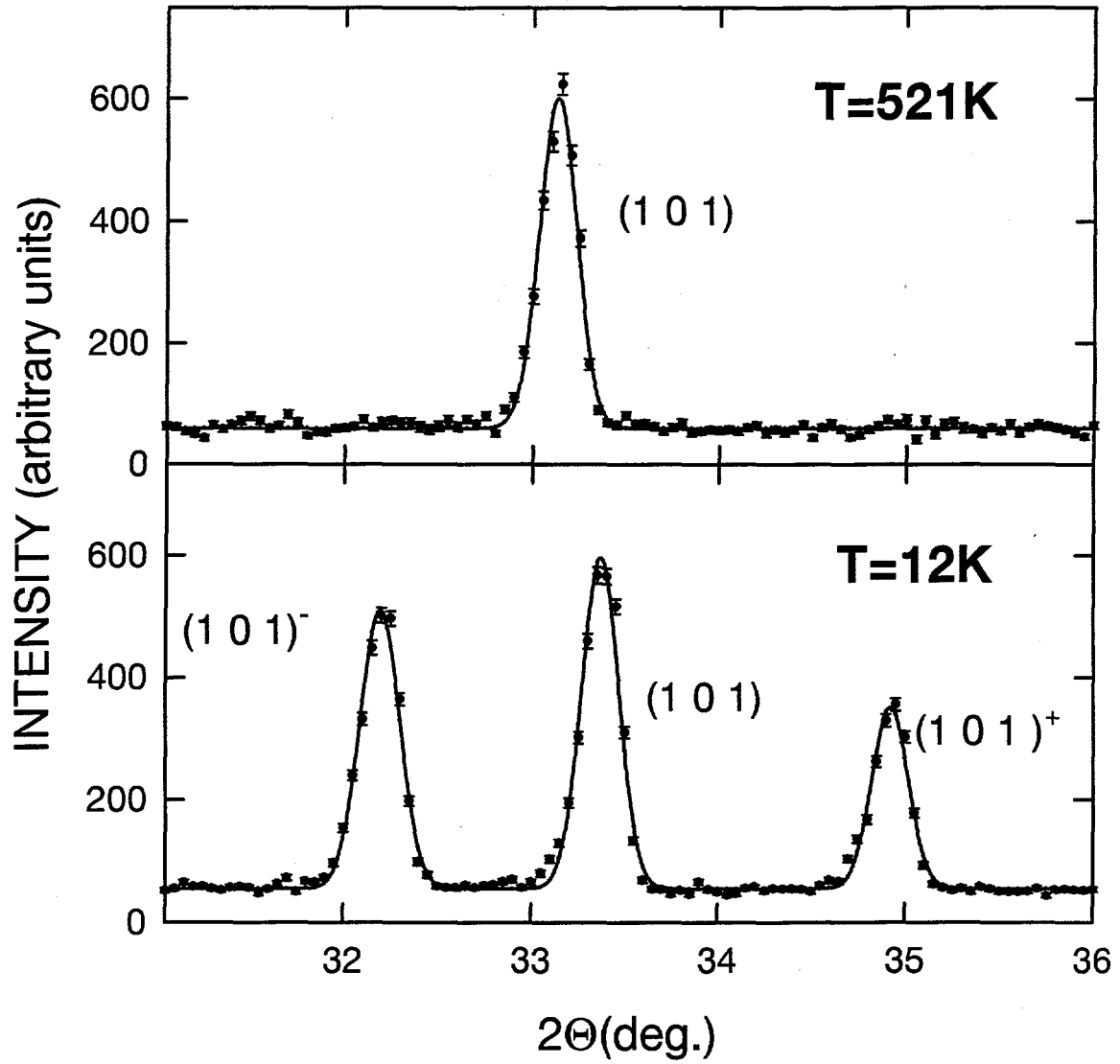


Figure 2

CeMn₂Ge₂

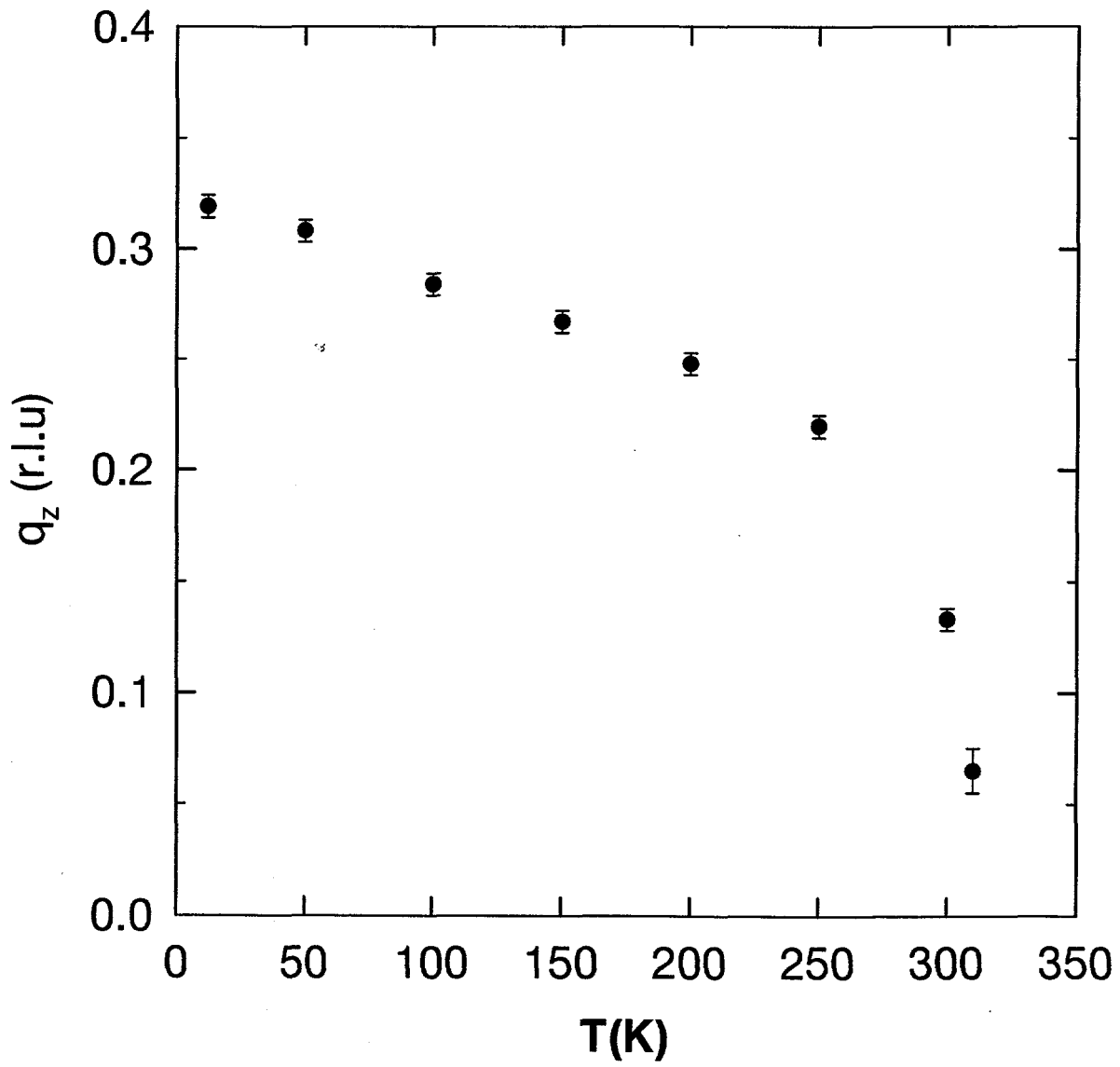


Figure 3